IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re the Application of:	)	Group Art Unit: 1762
Hampden-Smith et al.	)	Examiner: Brian K. Talbot
Serial No. 09/495,141	)	**APPEAL BRIEF (37 C.F.R. § 41.37)**
Filed: January 31, 2000	)	
Confirmation No. 4450	)	
Atty. File No.: 41890-00790 (Formerly SMP-023-2-1)	)	
For: "DIRECT-WRITE DEPOSITION OF PHOSPHOR POWDERS"	)	

Mail Stop Appeal Brief- Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

This Appeal Brief is being filed in relation to appeal of the above-identified U.S. Patent Application (hereinafter "the Application") from the final claim rejections stated in the Office Action dated April 24, 2006 (hereinafter "the Final Office Action").

This Appeal Brief includes the following appendices:

Appendix A – Claims;

Appendix B – Evidence; and

Appendix C – Related proceedings.

REAL PARTY IN INTEREST

The real party in interest is Cabot Corporation, Boston, MA, assignee of record of the Application.

RELATED APPEALS AND INTERFERENCES

None

STATUS OF CLAIMS

Claims 12-19, 24-27 and 29-42 are pending in the Application, Claims 1-11, 20-23 and 28 having been cancelled. Claims 12-19, 24-27 and 29-42 stand rejected under 35 U.S.C. § 103(a) and each of these claims is being appealed.

STATUS OF AMENDMENTS

For purposes of Appeal, the amendments submitted by Applicants in the Response to Office Action filed on September 25, 2006, have been entered and are reflected in Appendix A. The entry of these amendments was indicated by the Examiner in the Advisory Action mailed on November 9, 2006.

SUMMARY OF CLAIMED SUBJECT MATTER

The claims subject to appeal are directed to a method for depositing a phosphor pattern comprising phosphor particles on an article, such as a flat panel display, using a direct-write tool, such as an ink-jet device.

Independent **Claim 12**, directed to a method for depositing a phosphor pattern comprising phosphor particles on an article using a direct-write tool, recites the following steps:

providing a particulate suspension of phosphor particles having a viscosity of not greater than 30 centipoise (specification at page 47, lines 17-22), wherein the phosphor particles are substantially spherical (page 13, lines 31-32) and have a weight average particle size of from about 0.1 µm to about 20 µm (page 10, lines 1-3);

depositing said particulate suspension on an article using a direct-write tool that is controllable over an x-y grid (page 5, lines 29-32 and original Claim 12).

Claim 19 depends upon Claim 12, and Claim 19 is summarized as follows:

Claim 19: wherein said direct-write tool is selected from one of an automated syringe and an ink-jet device. (See, *inter alia,* page 5, line 29 to page 6, line 2 and original Claim 19).

Claims 13-18, 25-27, 29 and 39 all depend upon Claim 19, and each of these claims is summarized as follows:

Claim 13: wherein the average particle size is from about 0.3 µm to about 10 µm. (See, *inter alia,* page 10, lines 1-4 and original Claim 13);

Claim 14: wherein the particles comprise metal oxide phosphor particles. (See, *inter alia,* page 7, lines 29-33, and original Claim 14);

Claim 15: wherein the particles comprise metal sulfide phosphor particles. (See, *inter alia,* page 8, lines 18-25, and original Claim 15);

Claim 16: wherein the article is a panel for a flat panel display. (See, *inter alia,* page 51, lines 20-22 and original Claim 16);

Claim 17: wherein the phosphor particles have an apparent density of not greater than about 20 percent of the theoretical density of the phosphor compound. (See, *inter alia,* page 12, lines 1-4 and original Claim 17);

Claim 18: wherein said phosphor particles comprise hollow particles. (See, *inter alia,* page 12, lines 5-8, and original Claim 18).

Claim 25: wherein the phosphor particles have a size distribution wherein at least about 80 weight percent of the phosphor particles are not larger than twice the average particle size. (See, *inter alia,* page 10, lines 14-15);

Claim 26: wherein the phosphor particles have a size distribution wherein at least about 90 weight percent of the phosphor particles are not larger than twice said average particle size. (See, *inter alia,* page 10, lines 14-15);

Claim 27: wherein the particulate suspension comprises a water-based liquid vehicle. (See, *inter alia,* page 47, lines 28-31);

Claim 29: wherein the phosphor pattern comprises predetermined pixel regions. (See, *inter alia,* page 49, lines 24-26, Fig. 43).

Claim 39: wherein the direct-write tool is an automated syringe. (See, *inter alia,* page 5, line 33 to page 6, line 2).

Independent **Claim 24**, directed to a method for forming a flat panel display, recites the following steps:

a) providing a flat panel display screen (page 54, lines 20-31 and original Claim 24);

b) depositing at least first phosphor particles on the display screen, wherein said step of depositing comprises using a direct-write tool controllable over an x-y grid (page 5, lines 29-32) to deposit a liquid suspension having a viscosity of not greater than 30 centipoise (page 47, lines 17-22) and comprising said first phosphor particles in predetermined pixel regions to form pixels (page 54, lines 28-31 and Fig. 43) wherein said first phosphor particles have an average size of not greater than about 20 μm (page 10, lines 2-3) and a substantially spherical morphology (page 13, lines 31-32 and original Claim 24).

Claim 34 depends upon Claim 24, and is summarized as follows:

Claim 34: wherein the direct-write tool is selected from one of an ink-jet device and an automated syringe. (See, *inter alia,* page 5, line 29 to page 6, line 2 and original Claim 34).

Claims 30-33, 35-38 and 40 all depend upon Claim 34, and each of these claims is summarized as follows:

Claim 30: wherein the flat panel display is a field emission display. (See, *inter alia,* page 51, lines 31-32, Fig. 40, and original Claim 30);

Claim 31: wherein the flat panel display is a plasma display panel. (See, *inter alia,* page 53, line 6, Fig. 41 and original Claim 31);

Claim 32: wherein the phosphor particles have an average size of from about 0.3 μm to about 10 μm. (See, *inter alia,* page 10, lines 1-4, and original Claim 32);

Claim 33: further comprising the step of depositing at least second phosphor particles on the display screen, wherein said step of depositing comprises using the direct-write tool controllable over an x-y grid to deposit the second phosphor particles in the predetermined pixel regions wherein the second phosphor particles have an average size of not greater than about 20 μm and a substantially spherical morphology and have a composition different than the first phosphor particles. (See, *inter alia,* page 49, line 33 to page 50, line 12).

Claim 35: wherein the phosphor particles comprise metal oxide phosphor particles. (See, *inter alia,* page 7, lines 29-33);

Claim 36: wherein the phosphor particles comprise metal sulfide phosphor particles. (See, *inter alia,* page 8, lines 18-25);

Claim 37: wherein the phosphor particles have a size distribution wherein at least about 80 weight percent of the phosphor particles are not larger than twice the average particle size. (See, *inter alia,* page 10, lines 14-15);

Claim 38: wherein the phosphor particles have a size distribution wherein at least about 90 weight percent of the phosphor particles are not larger than twice the average particle size. (See, *inter alia,* page 10, lines 14-15).

Claim 40: wherein the direct-write tool is an automated syringe. (See, *inter alia,* page 5, line 33 to page 6, line 2).

Independent **Claim 41**, directed to a method for depositing a phosphor pattern comprising phosphor particles on an article using an ink-jet device, recites the following steps:

providing a particulate suspension of phosphor particles having a viscosity of not greater than 30 centipoise (page 47, lines 17-22), wherein the phosphor particles are substantially spherical (page 13, lines 31-32) and have a weight average particle size of from about 0.1 μm to about 20 μm (page 10, lines 1-3); and

depositing the particulate suspension on the article using an ink-jet device that is controllable over an x-y grid (page 5, lines 28-33).

Independent **Claim 42**, is directed to a method for forming a flat panel display, and recites the following steps:

a) providing a flat panel display screen (page 51, lines 20-22); and

b) depositing at least first phosphor particles on said display screen, wherein said step of depositing comprises using a ink-jet device controllable over an x-y grid to deposit a liquid suspension in predetermined pixel regions to form pixels (page 54, lines 28-31), said liquid suspension having a viscosity of not greater than 30 centipoise (page 47, lines 17-22)and comprising said first phosphor particles, wherein said first phosphor particles have an average size of not greater than about 20 μm (page 10, lines 1-3) and a substantially spherical morphology (page 13, lines 31-32).

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The following ground for rejection in the Final Office Action is to be reviewed in this Appeal:

Whether Claims 12-19, 24-27 and 29-42 are each unpatentable under 35 U.S.C. 103(a) as being obvious over U.S. Patent No. 6,100,633 by Okumura et al. (hereinafter "Okumura"), in combination with U.S. Patent No. 5,921,836 by Nanto et al. (hereinafter "Nanto"), further in combination with U.S. Patent No. 6,416,174 by Ito et al. (hereinafter "Ito").

ARGUMENT

1. Summary of Examiner's Position

The Examiner's position is that Okumura teaches: a plasma display panel with phosphor microspheres; the device can be a flat panel display; the phosphor particles can be of a particle size of 1 to 5 μm, and up to a particle size of 0.1 to 20 μm; the phosphor particles can comprise metal oxides or metal sulfides; and the phosphor particles are spherical in shape. The Examiner admits that Okumura fails to teach applying the phosphor in a pattern by a direct write tool controllable over an x-y axis.

The Examiner states that Nanto teaches an apparatus for forming fluorescent layers of a plasma display panel comprising a nozzle for ejecting the fluorescent layers, which is controllable over an x-y axis and that the dispenser is an automated syringe or nozzle.

The Examiner concludes that it would have been obvious for one skilled in the art at the time the invention was made to have modified the Okumura process by applying the phosphor material of Okumura with the apparatus of Nanto with the expectation of achieving more precise control over the desired deposition pattern. The Examiner admits that Okumura in combination with Nanto fail to teach applying the phosphor composition by a direct-write tool where the composition has a viscosity of less than 30 centipoise.

The Examiner states that Ito teaches an ink composition containing a solvent, a pigment (i.e., phosphor) dissolved in the solvent and a dispersant and that the ink composition has a surface tension of 20-50 dynes/cm and a viscosity of 1.5 to 20 centipoise. The Examiner also states that the pigment in the ink composition is comprised of particles and the ink composition can be applied to color filters, plasma displays, etc. by an ink-jet method.

The Examiner concludes that it would have been obvious for one skilled in the art at the time the invention was made to have modified Okumura in combination with Nanto by manipulating the phosphor composition to be applicable for ink-jet printing as evidenced by Ito with the advantages associated with the ink-jet process, i.e., more precise coating, increasing production, reduce cost, etc.

2. Summary of Applicants' Position

Applicants submit that there is no motivation or suggestion to combine the references to arrive at the present invention. Specifically, there is no motivation or suggestion to modify the combination of Okumura and Nanto by manipulating the phosphor composition to be applicable for ink-jet printing as evidenced by Ito.

3. Relevant Legal Doctrine

To establish a *prima facie* case of obviousness there must be some motivation, suggestion or teaching in the prior art that would lead a person of ordinary skill in the art to combine the references. More particularly:

> "[o]bviousness cannot be established by combining the teachings of the prior art to produce the claimed invention, absent some teaching or suggestion supporting the combination. Under section 103, teachings of references can be combined only if there is some suggestion or incentive to do so. Although couched in terms of combining teachings found in the prior art, the same inquiry must be carried out in the context of a purported obvious "modification" of the prior art. The mere fact that the prior art *may* be modified in the manner suggested by the Examiner does not make the modification obvious unless the prior art suggested the desirability of the modification." *In re Fritch*, 972 F.2d 1260, 1266 (Fed. Cir. 1992), emphasis added.

If a proposed modification would render the prior art invention being modified unsatisfactory for its intended purpose, *then there is no* suggestion or motivation to make the proposed modification. *In re Gordon*, 733 F.2d 900, 221 USPQ 1125 (Fed. Cir. 1984), emphasis added.

4. Claims 12-19, 25-27, 29 and 39

Independent Claim 12 recites a method that includes depositing a phosphor pattern comprising phosphor particles using a direct-write tool that is controllable over an x-y grid. A suspension of phosphor particles is provided having a viscosity of not greater than 30 centipoise, where the phosphor particles are substantially spherical and have a size of 0.1 μm to 20 μm. The suspension is deposited using the direct-write tool.

The method of Claim 12 provides many advantages as compared to other methods for the deposition of phosphor particles. Higher resolution displays can be produced, which is particularly important for small displays, such as the heads-up displays used in aircraft. The total amount of phosphor powder needed to construct the display can also be reduced, and the manufacturing process can be automated using CAD/CAM techniques. See, for example, page 55, lines 20-30 of the present specification.

Applicants submit that one of ordinary skill in the art would have no motivation to combine teachings regarding phosphor paste deposition (Okumura and Nanto) with teachings regarding the suspension of pigments for use in an ink-jet to fabricate color filters in a display device (Ito).

Both Okumura and Nanto employ paste for the deposition of phosphor particles. See, for example, Okumura at: Col. 5, lines 5-10; Example 1, Col. 8, lines 40-48; and Example 1b, Col. 9, lines 20-25. Also, see Nanto at: Abstract; Col. 1, line 47-57; and Col. 4, lines 16-25. The term paste, as used by Okumura and Nanto, refers to relatively viscous compositions that are deposited using methods such as screen printing (e.g., Okumura at Col. 5, lines 9-11). Phosphor pastes (such as those disclosed by Okumura and Nanto) have a viscosity that is much higher than 30 centipoise. As is disclosed in the present specification at page 2, lines 5-15, the use thick-film pastes is not desired due to the necessary complicated and labor-intensive production steps that are required.

The apparatus of Nanto includes a dispenser having a nozzle for ejecting the paste while the nozzle is moved relative to the plasma display panel. The paste is applied into grooves that are formed between a plurality of ribs that are disposed in parallel relation on the surface of the substrate (e.g., the Abstract). Fluorescent layers are formed in each of the grooves between adjacent ribs by letting the fluorescent paste eject from the tip of the nozzle while the tip of the nozzle is moved relative to the substrate (Col. 5, lines 7-10). The inner diameter of the nozzle utilized by Nanto is about 100 μm in diameter (Col. 4, lines 26-39).

The Examiner's suggestion is that the paste of Okumura (including spherical particles) could be utilized in the apparatus of Nanto, and *then* one of ordinary skill in the art would be motivated to somehow reduce the viscosity of the paste of Okumura to less than

30 centipoise, based solely upon the teachings of Ito. Applicants submit that such a combination is improper and cannot stand.

Ito is directed to the deposition of an ink composition having pigment in it droplets to form a colored layer of a color filter on the surface of a base material (e.g., the Abstract). Although phosphor materials are disclosed (Col. 7, lines 46-47), the application is for a color filter layer, not for a phosphorescent layer. For example, the layer can be used in an LCD device, which does not even include phosphors. Thus, a skilled artisan would not be motivated to modify a paste composition for a phosphor layer in a flat panel display (Okumura), that is deposited using a nozzle (Nanto), by reducing the viscosity based on the teachings of Ito.

Further, a suspension of particles having a viscosity of less than 30 centipoise (e.g., Ito) would not be useful in the apparatus of Nanto, given the nature of the apparatus used by Nanto. This is illustrated by the large diameter of the nozzle (>100 μm) used by Nanto. Such a low viscosity composition could not be ejected through the nozzle of Nanto without significant flow control problems. Thus, the combination suggested by the Examiner would render the method unsatisfactory for its intended purpose and, therefore, there is no motivation to combine the references.

5. Claims 24, 30-38 and 40

Independent Claim 24 requires that the method includes providing a flat panel display screen and depositing at least first phosphor particles in pixel regions to form pixels. None of the cited references disclose the formation of pixels.

Applicants submit that the Examiner has not shown the required motivation to combine the references to arrive at the claimed invention, as is discussed in detail above with respect to independent Claim 12. These arguments apply equally to independent Claim 24.

Further, neither Okumura nor Nanto disclose depositing phosphor particles in pixel regions to form pixels. Rather, Okumura and Nanto disclose the continuous deposition of phosphor particles into a plurality of adjacent grooves. Portions of the grooves are

addressed to illuminate phosphor particles by corresponding address electrodes and sustaining electrodes.

Ito is directed to the deposition of a color pigment for display applications. The pigments are not deposited to form pixel regions but rather are deposited to form a color filter for display such as a CRT, an LCD or a plasma display. (Col. 1, lines 31-35).

Thus, none of the references, alone or in any combination, disclose the formation of pixel regions by the deposition of phosphor particles, as is required by independent Claim 24.

6. Independent Claim 41

Independent Claim 41 recites a method wherein a phosphor pattern is deposited onto an article using an ink-jet device that is controllable over an x-y grid. A particulate suspension is deposited, where the particulate suspension includes spherical phosphor particles and the suspension has a viscosity of not greater than 30 centipoise.

As is discussed above in detail with respect to independent Claim 12, one of ordinary skill in the art would have no motivation to combine teachings regarding phosphor paste deposition (Okumura and Nanto) with teachings regarding the suspension of pigments for use in an ink-jet to fabricate color filters in a display device (Ito).

Further, the Examiner has not demonstrated how the composition of Okumura, as modified by Ito and deposited by the device of Nanto, encompasses the deposition of spherical phosphors using an ink-jet device. Although the Examiner states that the composition of Ito can be deposited by an ink-jet method, the Examiner has not demonstrated any reasoning, based on the prior art of record, as to why it would be obvious to substitute an ink-jet device for the apparatus of Nanto. Applicants submit that it would not be obvious, since the apparatus of Nanto requires a paste composition for operation, and a paste composition cannot be deposited using an ink-jet device.

7. Independent Claim 42

Independent Claim 42 is recites a method for forming a flat panel display that includes depositing phosphor particles on a display screen. An ink-jet device is used to deposit a low viscosity suspension of spherical phosphor particles in predetermined pixel

regions to form pixels.

As is discussed above with respect to independent Claim 12, the Examiner has shown no motivation for modifying the composition of Okumura by reducing the viscosity of the composition and depositing it using the device of Nanto. As is also discussed above with respect to independent Claim 41, the Examiner has shown no line of reasoning to conclude that an ink-jet device can be substituted for the apparatus of Nanto. Further, none of the references disclose depositing phosphor particles in predetermined pixel regions to form pixels.

8. Dependent Claims 17 and 18

With respect to the dependent claims reciting densities (dependent Claim 17) and the particles being hollow (dependent Claim 18), the Examiner's position is that these factors are "result effective variables" which are optimized through routine experimentation depending on the desired final product, and that optimizing a well known result effective variable is deemed an obvious modification of the art, absent a showing of unexpected results. The Examiner has cited no precedent for this proposition.

A particular parameter must be first recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation. *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977), as cited at MPEP 2144.05, Section IIB. For example, *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980), also cited at MPEP 2144.05, Section IIB, is an illustrative case where the applicants were claiming a nickel alloy composition. The nickel alloy composition included Cr, Mo and Co and a specific compositional relationship was claimed for the relative concentrations of these elements in the alloy (namely, that N·v ≤ 2.35, where N·v is calculated from a formula based on the concentrations of Cr, Mo and Ni in the alloy). . However, the court made a specific finding that the relationship among these elements (i.e., the N·v formula) was known and furthermore that "the higher the N·v value of a Co-Cr-Ni alloy, the higher the chance for precipitation of embrittling phases" – thus, minimizing the N·v value was also taught, for the very same reasons set forth by the applicants (namely, to avoid the formation of a deleterious phase in the metal). Thus, the prior art taught "the kind of

experimentation necessary to achieve the claimed composition, including the proportional balancing described by [applicants] N·v equation." *Boesch*, at 276.

In contrast, there is no such disclosure or suggestion in any of the cited references that these parameters are "result-effective variables" that should be optimized, nor is there a suggestion as to *how* these variables should be optimized. Indeed, it is unclear to Applicants how the recitation of "hollow particles" can be considered a variable at all. Therefore, it is submitted that these dependent claims further distinguish the claimed invention over the cited references.

9. Dependent Claim 29

Dependent Claim 29 depends upon Claim 19, which depends upon independent Claim 12. In addition to the foregoing discussion relating to independent Claim 12, dependent Claim 29 requires that the phosphor pattern comprises predetermined pixel regions. As is discussed above with respect to independent Claim 24, none of the cited references disclose the formation of a phosphor pattern comprising predetermined pixel regions.

The fee under 37 CFR §41.20(b)(2) accompanies this Appeal Brief. Please charge any underpayment or credit any overpayment to Deposit Account No. 50-1419.

Respectfully submitted,

MARSH FISCHMANN & BREYFOGLE LLP

By: /David F Dockery Reg No 34323/
David F. Dockery
Registration No. 34,323
3151 South Vaughn Way, Suite 411
Aurora, Colorado 80014
(303) 338-0997

Date: December 26, 2006

APPENDIX A

<u>Listing of Claims</u>:

Claims 1-11 (Cancelled)

12. (Appealed) A method for depositing a phosphor pattern comprising phosphor_particles on an article using a direct-write tool, comprising the steps of:

providing a particulate suspension of said phosphor particles having a viscosity of not greater than 30 centipoise, wherein said phosphor particles are substantially spherical and have a weight average particle size of from about 0.1 μm to about 20 μm; and

depositing said particulate suspension on said article using a direct-write tool that is controllable over an x-y grid.

13. (Appealed) A method as recited in Claim 19, wherein said average particle size is from about 0.3 μm to about 10 μm.

14. (Appealed) A method as recited in Claim 19, wherein said particles comprise metal oxide phosphor particles.

15. (Appealed) A method as recited in Claim 19, wherein said particles comprise metal sulfide phosphor particles.

16. (Appealed) A method as recited in Claim 19, wherein said article is a panel for a flat panel display.

17. (Appealed) A method as recited in Claim 19, wherein said phosphor particles have an apparent density of not greater than about 20 percent of the theoretical density of the phosphor compound.

18. (Appealed) A method as recited in Claim 19, wherein said phosphor

particles comprise hollow particles.

19. (Appealed) A method as recited in Claim 12, wherein said direct-write tool is selected from one of an automated syringe and an ink-jet device.

Claims 20-23. (Cancelled)

24. (Appealed) A method for forming a flat panel display, comprising the steps of:

a) providing a flat panel display screen;

b) depositing at least first phosphor particles on said display screen, wherein said step of depositing comprises using a direct-write tool controllable over an x-y grid to deposit a liquid suspension having a viscosity of not greater than 30 centipoise and comprising said first phosphor particles in predetermined pixel regions to form pixels wherein said first phosphor particles have an average size of not greater than about 20 μm and a substantially spherical morphology.

25. (Appealed) A method as recited in Claim 19, wherein said phosphor particles have a size distribution wherein at least about 80 weight percent of said phosphor particles are not larger than twice said average particle size.

26. (Appealed) A method as recited in Claim 19, wherein said phosphor particles have a size distribution wherein at least about 90 weight percent of said phosphor particles are not larger than twice said average particle size.

27. (Appealed) A method as recited in Claim 19, wherein said particulate suspension comprises a water-based liquid vehicle.

28. (Cancelled)

29. (Appealed) A method as recited in Claim 19, wherein said phosphor pattern comprises predetermined pixel regions.

30. (Appealed) A method as recited in Claim 34, wherein said flat panel display is a field emission display.

31. (Appealed) A method as recited in Claim 34, wherein said flat panel display is a plasma display panel.

32. (Appealed) A method as recited in Claim 34, wherein said phosphor particles have an average size of from about 0.3 μm to about 10 μm.

33. (Appealed) A method as recited in Claim 34, further comprising the step of depositing at least second phosphor particles on said display screen, wherein said step of depositing comprises using said direct-write tool controllable over an x-y grid to deposit said second phosphor particles in said predetermined pixel regions wherein said second phosphor particles have an average size of not greater than about 20 μm and a substantially spherical morphology and have a composition different than said first phosphor particles.

34. (Appealed) A method as recited in Claim 24, wherein said direct-write tool is selected from one of an ink-jet device and an automated syringe.

35. (Appealed) A method as recited in Claim 34, wherein said phosphor particles comprise metal oxide phosphor particles.

36. (Appealed) A method as recited in Claim 34, wherein said phosphor particles comprise metal sulfide phosphor particles.

37. (Appealed) A method as recited in Claim 34, wherein said phosphor particles have a size distribution wherein at least about 80 weight percent of said phosphor particles are not larger than twice said average particle size.

38. (Appealed) A method as recited in Claim 34, wherein said phosphor particles have a size distribution wherein at least about 90 weight percent of said phosphor particles are not larger than twice said average particle size.

39. (Appealed) A method as recited in Claim 19 wherein said direct-write tool is an automated syringe.

40. (Appealed) A method as recited in Claim 34, wherein said direct-write tool is an automated syringe.

41. (Appealed) A method for depositing a phosphor pattern comprising phosphor particles on an article using an ink-jet device, the method comprising the steps of:

providing a particulate suspension of said phosphor particles having a viscosity of not greater than 30 centipoise, wherein said phosphor particles are substantially spherical and have a weight average particle size of from about 0.1 μm to about 20 μm; and

depositing said particulate suspension on said article using an ink-jet device that is controllable over an x-y grid.

42. (Appealed) A method for forming a flat panel display, comprising the steps of:

a) providing a flat panel display screen; and

b) depositing at least first phosphor particles on said display screen, wherein

said step of depositing comprises using a ink-jet device controllable over an x-y grid to deposit a liquid suspension in predetermined pixel regions to form pixels, said liquid suspension having a viscosity of not greater than 30 centipoise and comprising said first phosphor particles, wherein said first phosphor particles have an average size of not greater than about 20 μm and a substantially spherical morphology.

APPENDIX B

Evidence

1. U.S. Patent No. 6,100,633 by Okumura et al.
2. U.S. Patent No. 5,921,836 by Nanto et al.
3. U.S. Patent No. 6,416,174 by Ito et al.

US006100633A

United States Patent [19]

Okumura et al.

[11] **Patent Number: 6,100,633**

[45] **Date of Patent: Aug. 8, 2000**

[54] **PLASMA DISPLAY PANEL WITH PHOSPHOR MICROSPHERES**

[75] Inventors: **Miwa Okumura**, Kawasaki; **Naotoshi Matsuda**, Tokyo; **Masaaki Tamatani**, Fujisawa; **Ariane Keiko Albessard**, Yokohama, all of Japan

[73] Assignee: **Kabushiki Kaisha Toshiba**, Kawasaki, Japan

[21] Appl. No.: **08/939,491**

[22] Filed: **Sep. 29, 1997**

[30] **Foreign Application Priority Data**

Sep. 30, 1996 [JP] Japan 8-258508

[51] **Int. Cl.**[7] **H01J 63/04**

[52] **U.S. Cl.** .... **313/486**; 313/113; 313/584; 252/301.4 R

[58] **Field of Search** .... 313/467, 468, 313/486, 487, 112, 113, 114, 584, 585, 586; 252/301.4 R, 301.5

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,995,191	11/1976	Kaduk et al.	313/113
4,803,402	2/1989	Raber et al.	313/586
4,827,186	5/1989	Knauer et al.	313/486
5,182,489	1/1993	Sano	313/585
5,214,345	5/1993	Saito et al.	313/112
5,442,254	8/1995	Jaskie	313/486
5,644,193	7/1997	Matsuda et al.	313/486
5,811,924	9/1998	Okumura et al.	313/467

FOREIGN PATENT DOCUMENTS

5-61080	3/1993	Japan	G02F 1/35
7-320645	12/1995	Japan	H01J 11/02
8-092553	4/1996	Japan	C09K 11/68
8-092554	4/1996	Japan	C09K 11/84
8-109375	4/1996	Japan	C09K 11/78
8-134443	5/1996	Japan	C09K 11/78

OTHER PUBLICATIONS

C. G. B. Garrett, et al., "Stimulated Emission into Optical Whispering Modes of Spheres", Physical Review, vol. 124, No. 6, Dec. 15, 1961, pp. 1807–1857.

K. Miura, et al., "Laser Oscillation of a Nd^{3+}–Doped Fluoride Glass Microsphere", Journal of Materials Science Letters 15 (1996), pp. 1854–1857.

T. Akiyama, et al., "Evaluations of Discharge Cell Structure for Color AC Plasma Display Panels", Abstract of the 261st meeting of Phosphor Society of Japan, (1996), p. 1.

Abstract of the 267th meeting of Phosphor Society of Japan (1997), pp. 5–13, (no month).

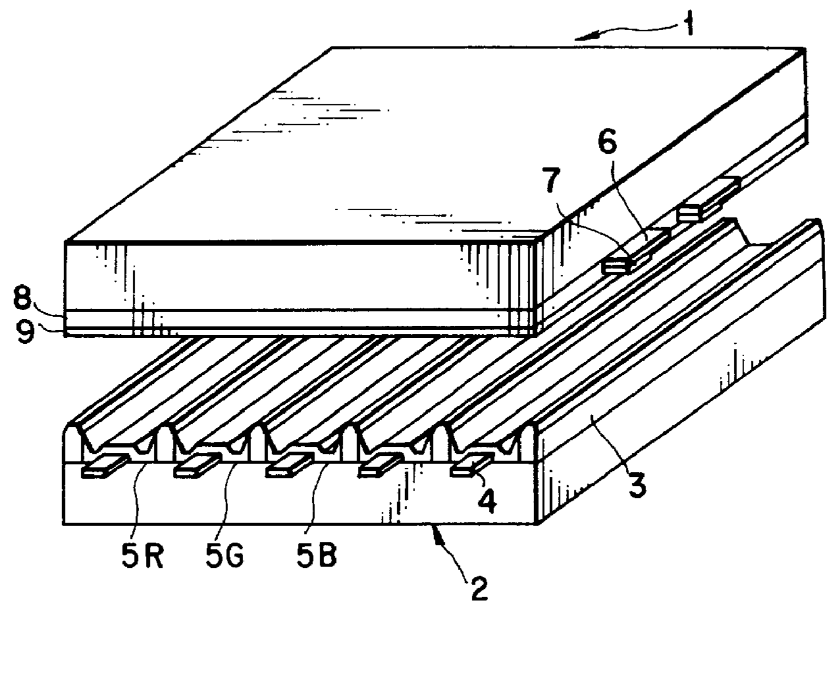
Primary Examiner—Michael Day

Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

The present invention provides a plasma display panel, comprising a rear substrate provided with ribs defining discharge cells, address electrodes and phosphor layers, and a front substrate provided with transparent electrodes extending in a direction perpendicular to the address electrodes, a transparent dielectric layer and a protective layer, discharge being brought about within the discharge cell formed between the rear substrate and the front substrate to excite the phosphor contained in the phosphor layer so as to cause the phosphor to emit a visible light. In this plasma display panel, the phosphor particles forming the phosphor layer have an average particle size of 0.1 to 5 μm and a ratio of the largest curvature to the smallest curvature of at most 1.5. Also, the magnitude of the irregularities on the surface of the phosphor particle is at most 5% of the diameter of the phosphor particle.

9 Claims, 4 Drawing Sheets



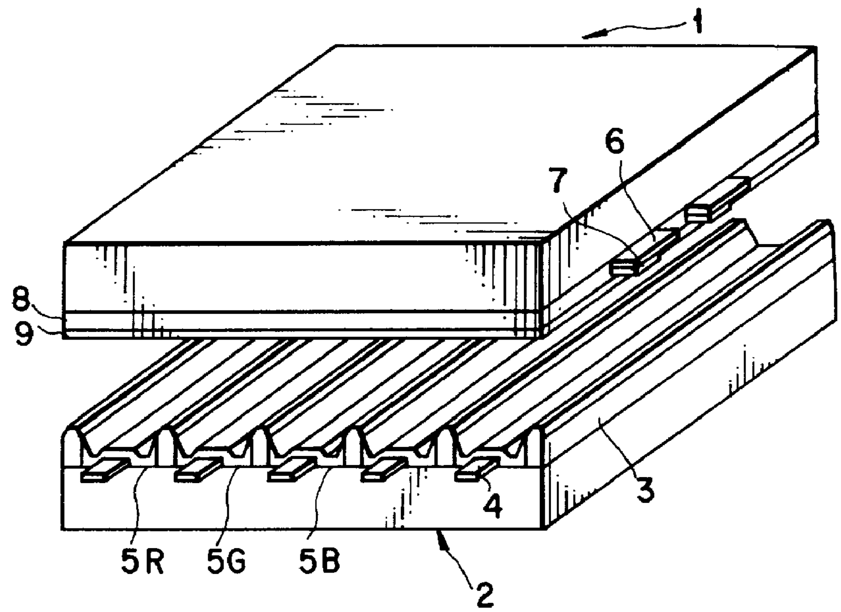


FIG. 1

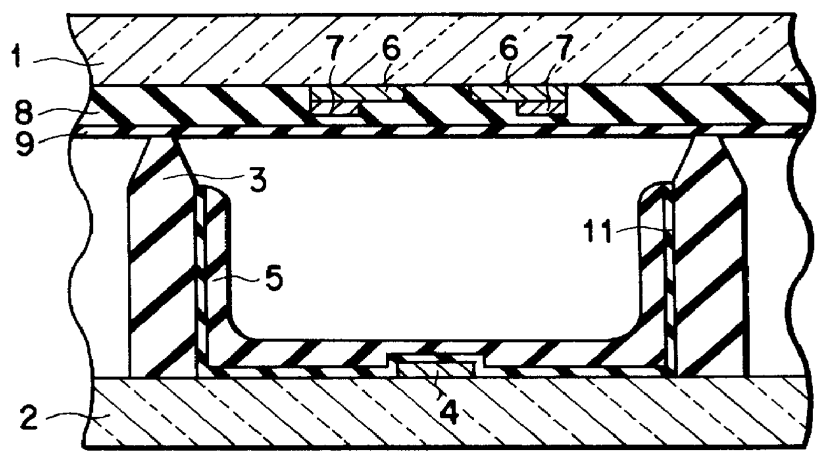


FIG. 2

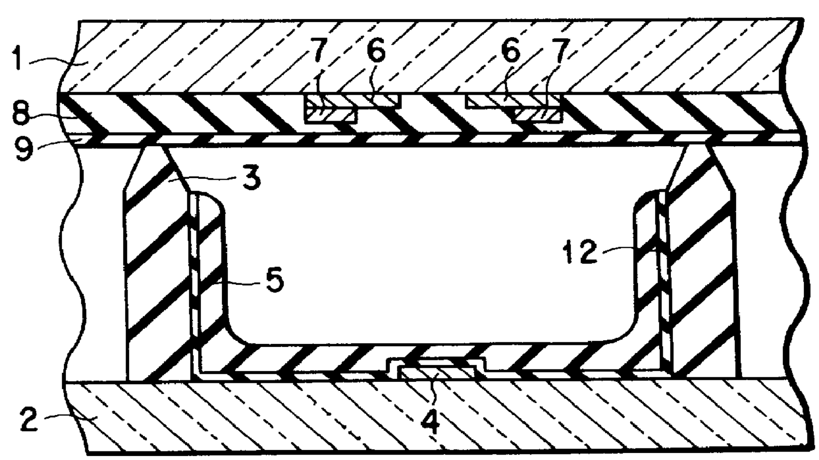


FIG. 3

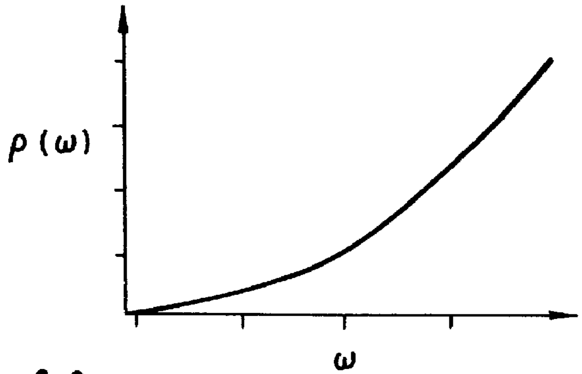


FIG. 4A

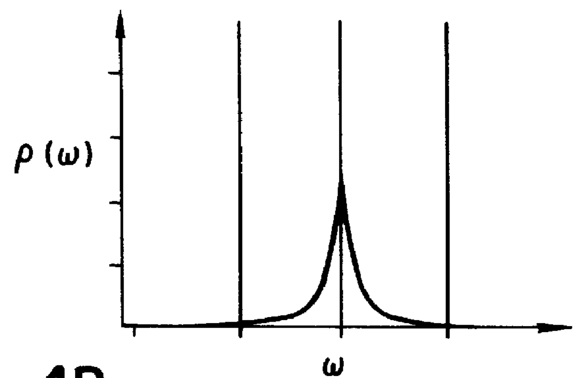


FIG. 4B

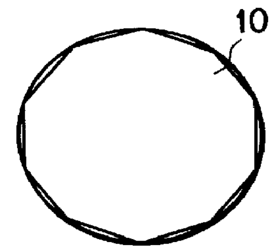


FIG. 4C

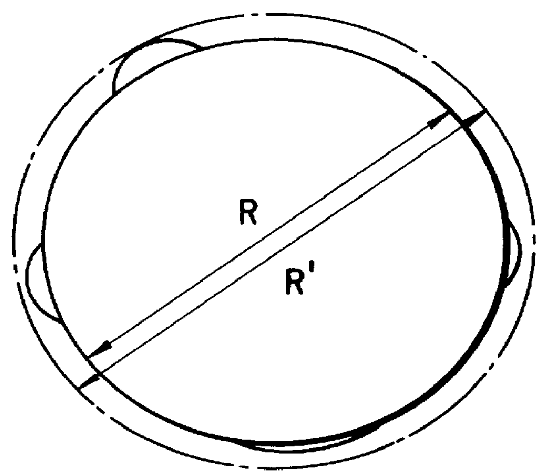


FIG. 5

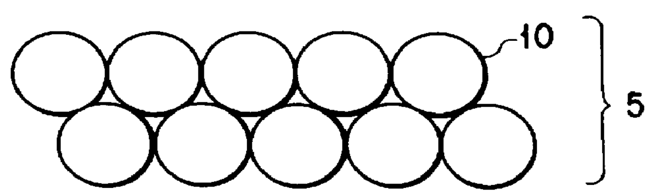


FIG. 6

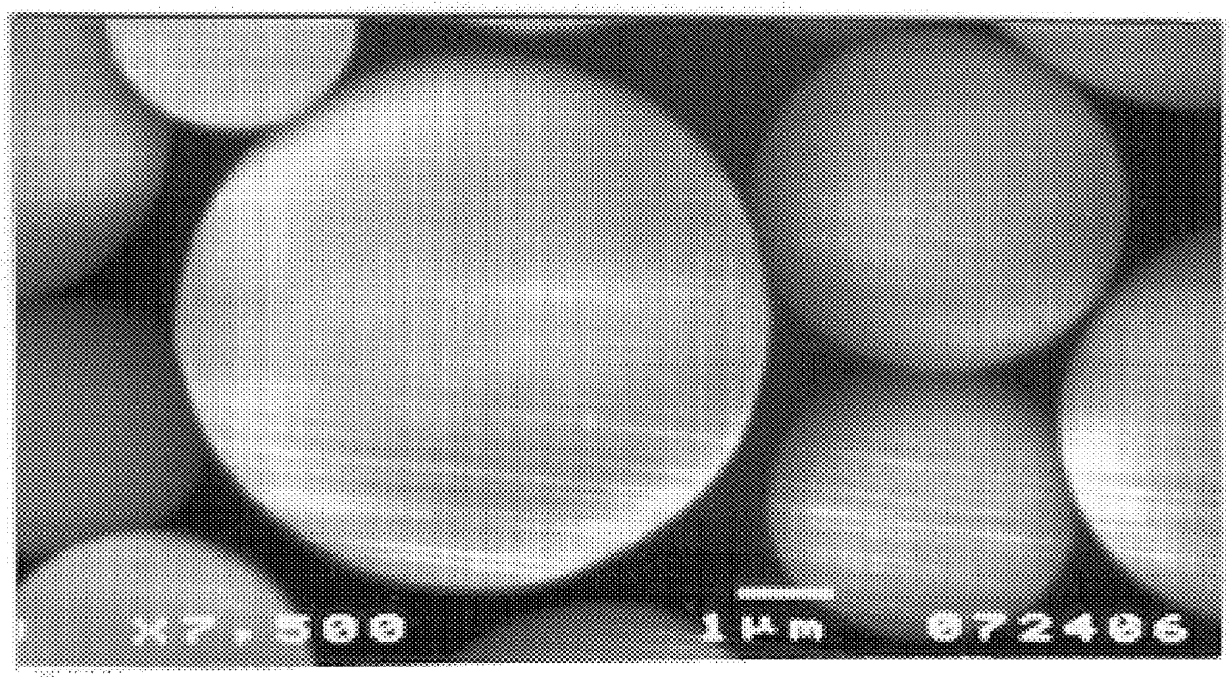


FIG. 7

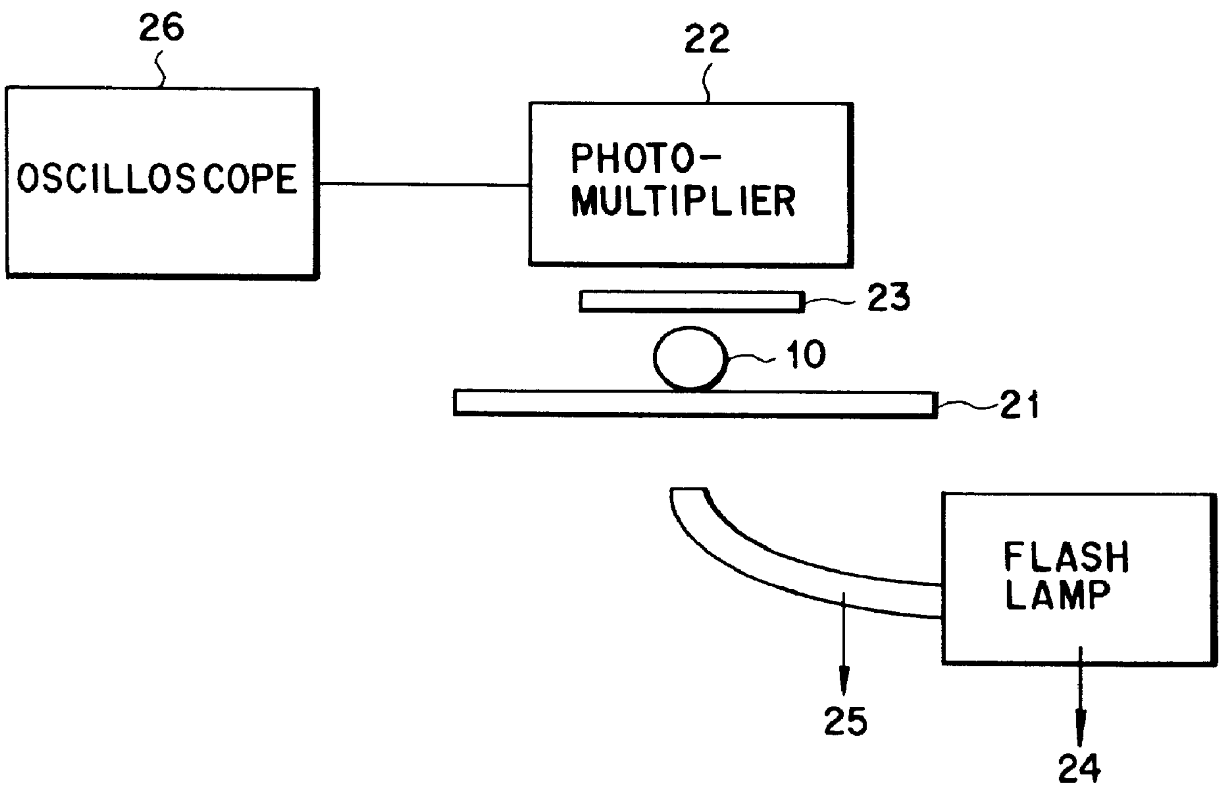

26
OSCILLOSCOPE
22
PHOTO-
MULTIPLIER
23
10
21
FLASH
LAMP
25
24

FIG. 8

PLASMA DISPLAY PANEL WITH PHOSPHOR MICROSPHERES

BACKGROUND OF THE INVENTION

The present invention relates to a plasma display panel (PDP) and a phosphor adapted for use in various displays such as PDP.

The plasma display panel (PDP), which is adapted for preparation of a large screen and can be made thinner, attracts attention as a flat display panel which can be used in place of a cathode ray tube (CRT).

A surface discharge AC type PDP comprises a rear substrate provided with ribs defining discharge cells, address electrodes formed in the discharge cells and phosphor layers, and a front substrate provided with transparent electrodes extending in a direction perpendicular to the address electrodes, a transparent dielectric layer and a protective layer. The phosphor layer is formed by coating the discharge cells by means of, for example, a screen printing technique, with a paste of phosphor particles emitting red (R), green (G) or blue (B) lights, followed by drying the coating. Thickness of the phosphor layer is set at about 20 μm. A mixed gas such as He—Xe or Ne—Xe is sealed as a discharge gas in the discharge cell formed between the rear substrate and the front substrate. In the PDP of this type, a surface discharge is brought about in the vicinity of the front substrate within the discharge cells. As a result, ultraviolet light is generated from the discharge gas sealed in the discharge cell, and the generated ultraviolet light excites the phosphor so as to permit the phosphor to emit a visible light.

It was customary in the past to form the phosphor layer of the PDP by using the phosphor prepared by the firing method using a flux. The phosphor particles prepared by this method are polyhedral. It should be noted that polyhedral phosphor particles are poor in dispersion capability. Therefore, if used for preparing a phosphor paste, the polyhedral phosphor particles tend to aggregate, giving rise to serious problems. For example, voids are generated within the phosphor layer, if a phosphor layer is formed by coating the paste. As a result, the thickness of the phosphor layer is increased so as to diminish the discharge space of the cell and, thus, to decrease the ultraviolet light serving to excite the phosphor. It follows that the brightness of the PDP is lowered. It should also be noted that, if a phosphor layer is formed by coating the paste containing polyhedral phosphors, the phosphor layer surface becomes irregular. Since the irregular surface of the phosphor layer brings about irregular reflection of light, the light loss is increased so as to lower the brightness. In addition, the brightness is rendered nonuniform over the entire region of the phosphor screen. As a matter of fact, the brightness of the PDP available on the market is 0.8 [lm/W] in terms of the entire efficiency in contrast to 1.7 [lm/W] for the CRT.

In order to increase the brightness of the PDP, various measures have been taken to date, including, for example the measures given below:

(1) Phosphor particles having a particle size of at most 1.5 μm should be used for forming a phosphor layer;

(2) The thickness of the phosphor layer should be gradually increased towards the front substrate; and

(3) A white reflective layer consisting of titanium oxide should be formed below the phosphor layer.

However, any of these measures fails to essentially resolve the problem of the reduced brightness caused by the diminished discharge space resulting from the increased thickness of the phosphor layer and by the irregular reflection of light resulting from the irregular surface of the phosphor layer. Of course, it is of high importance to improve the brightness of the PDP.

It should also be noted that the conventional PDP is low in response speed, giving rise to a problem that an afterimage is generated in the case of displaying a moving picture. Particularly, a Zn_2SiO_4:Mn phosphor widely used as a green-emitting phosphor has a long life and, thus, is likely to generate a green afterimage. Naturally, it is also of high importance to suppress generation of an afterimage in the PDP.

BRIEF SUMMARY OF THE INVENTION

An object of the present invention is to provide a plasma display panel which exhibits a high brightness and is unlikely to generate an afterimage. Another object is to provide a phosphor exhibiting a high quantum efficiency, having a short emission life time, and contributing to the improvement of the display performance.

According to an aspect of the present invention, there is provided a plasma display panel, comprising a rear substrate provided with ribs defining discharge cells, address electrodes and a phosphor layer, and a front substrate provided with transparent electrodes extending in a direction perpendicular to the address electrodes, a transparent dielectric layer and a protective layer, discharge being brought about within the discharge cell formed between the rear substrate and the front substrate to excite the phosphor contained in the phosphor layer so as to cause the phosphor to emit a visible light, wherein the phosphor particles forming the phosphor layer have an average particle size of 0.1 to 5 μm and an aspect ratio of 1.0 to 1.5.

According to another aspect of the present invention, there is provided a plasma display panel, comprising a rear substrate provided with ribs defining discharge cells, address electrodes and a phosphor layer, and a front substrate provided with transparent electrodes extending in a direction perpendicular to the address electrodes, a transparent dielectric layer and a protective layer, discharge being brought about within the discharge cell formed between the rear substrate and the front substrate to excite the phosphor contained in the phosphor layer so as to cause the phosphor to emit a visible light, wherein the phosphor particles forming the phosphor layer have an average particle size of 0.1 to 5 μm and a ratio of the largest curvature to the smallest curvature of at most 1.5.

The phosphor of the present invention has an average particle size falling within a range of between 0.1 μm and 20 μm and exhibits a so-called "microresonator effect". Also, the surface roughness of the phosphor is not larger than 5% of the particle size.

Additional object and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The object and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention, and together with the general description given above and the detailed descrip-

tion of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. **1** is an exploded view of a surface discharge AC type plasma display panel (PDP) according to the present invention;

FIG. **2** is a cross sectional view showing a PDP provided with a reflective layer of a visible light;

FIG. **3** is a cross sectional view showing a PDP provided with a reflective layer of an ultraviolet light;

FIG. **4A** is a graph showing the dependency of the density of states on frequency in the case where spontaneous emission is taking place;

FIG. **4B** is a graph showing the dependency of the density of states on frequency in the case where a microresonator effect is taking place;

FIG. **4C** shows a microresonator effect;

FIG. **5** shows how to calculate the surface roughness of a phosphor particle;

FIG. **6** shows a phosphor layer having a thickness two times as large as the average particle size of phosphor particles;

FIG. **7** is an SEM photograph showing the phosphor particles obtained in Example 2a of the present invention; and

FIG. **8** shows the construction of an apparatus used for measuring the brightness and the emission life time of the phosphor particles.

DETAILED DESCRIPTION OF THE INVENTION

FIG. **1** shows the construction of a surface discharge AC type plasma display panel (PDP) according to the present invention. As shown in the drawing, the PDP comprises a front substrate **1** and a rear substrate **2**. Ribs **3** arranged in parallel to form stripes are formed on the rear substrate **2** in a manner to define stripe-like discharge cells. Also, stripe-like address electrodes **4** are formed between adjacent ribs **3** such that each discharge cell formed between adjacent ribs **3** is provided with the address electrode **4**. Further, phosphor layers **5** are formed which cover the surfaces of the rear substrate **2**, address electrodes **4** and ribs **3**. The phosphor layer **5** contains a red-emitting phosphor, a green-emitting phosphor or a blue-emitting phosphor. On the other hand, formed on the front substrate **6** are stripe-like transparent electrodes **6** extending in a direction perpendicular to the address electrodes **4** and bus electrodes **7** overlapping with the transparent electrodes **7** to lower the resistance of the transparent electrodes **7**. The surface of the front substrate **1** is covered with a transparent dielectric layer **8** and a protective layer **9**. The protective layer **9** consisting of, for example, MgO serves to improve the discharge characteristics. The front substrate **1** of the particular construction is disposed on the rear substrate **2** of the construction described above, followed by sealing the junction between the front and rear substrates. Further, a mixed gas such as He—Xe or Ne—Xe is sealed as a discharge gas in the discharge cells formed between the rear substrate **2** and the front substrate **1**.

The surface discharge AC type PDP of the construction described above is operated as follows. Specifically, if a surface discharge is brought about in the vicinity of the front substrate within the discharge cell, the discharge gas sealed in the discharge cell emits vacuum ultraviolet (VUV) rays having wavelengths of mainly 147 nm and 172 nm. As a result, the phosphor in the phosphor layer is excited by the vacuum ultraviolet rays and emits a visible light when the excited state is brought back to the ground state.

The phosphor layer **5** contains phosphors exemplified below, though the phosphors used in the present invention are not limited to those exemplified below. Specifically, the red-emitting phosphors used in the present invention include, for example, Y_2O_3:Eu, $(Y, Gd)_2O_3$:Eu, Y_2SiO_5:Eu, YBO_3:Eu, $(Y,Gd)BO_3$:Eu, $GdBO_3$:Eu, and $ScBO_3$:Eu. The green-emitting phosphors used in the present invention include, for example, $BaAl_{12}O_{19}$:Mn, YBO_3:Tb, and Zn_2SiO_4:Mn. Further, the blue-emitting phosphors used in the present invention include, for example, $BaMgAl_{14}O_{23}$:Eu^{+2}, $CaWO_4$:Pb and Y_2SiO_5:Ce.

Transparent phosphor particles, which are substantially spherical and substantially free from projections such as edges on the surfaces, are used for forming the phosphor layer included in the PDP of the present invention. To be more specific, the phosphor particles should have an average particle size of 0.1 to 5 μm, preferably 0.5 to 1 μm, and an aspect ratio, i.e., a ratio of the longest diameter to the shortest diameter, of 1.0 to 1.5. If the average particle size of the phosphor particles is less than 0.1 μm, the brightness of the phosphor screen is low. Where the average particle size exceeds 5 μm, however, the phosphor layer formed by coating tends to have an irregular surface. The aspect ratio of the phosphor particles, which should be 1.0 to 1.5, should preferably be 1.0 to 1.2 and, more preferably 1.0 to 1.1. Where the aspect ratio of the phosphor particles exceeds 1.5, the phosphor layer formed by coating of the phosphor particles tends to have an irregular surface.

If a paste is prepared by using the spherical phosphor particles defined in the present invention, the phosphor particles are sufficiently dispersed in the paste, with the result that the phosphor particles are not aggregated together so as to lower the viscosity of the resultant paste. Where a phosphor layer is formed by coating the particular paste, void formation within the phosphor layer is suppressed. Also, the phosphor layer is allowed to have a smooth surface free from irregularity. It follows that the packing density can be increased by 50 to 65% compared with the case where conventional phosphor particles are used. As a result, it is possible to prevent an irregular reflection of the light emitted from the phosphor so as to suppress loss of light and, thus, to improve the brightness of the PDP. Also, the smooth surface of the phosphor layer permits enlarging the discharge space, which also contributes to an improvement of the brightness.

The spherical phosphor particles used in the present invention can be prepared by, for example, melting raw material phosphor particles within a heat plasma, followed by rapidly cooling the melt. A method of preparing spherical phosphor particles by utilizing a heat plasma is disclosed in, for example, Japanese Patent Disclosure (Kokai) No. 8-109375. It is also possible to prepare spherical phosphor particles by means of plasma spray coating.

Particularly, where the PDP is required to exhibit a high emission efficiency and a high accuracy in the color of the emitted light, it is desirable to use spherical phosphor particles having chromaticity coordinates (x, y), which is used as an index of whiteness degree, of:

$$0.31 \leqq x \leqq 0.33$$

$$0.31 \leqq y \leqq 0.33$$

The phosphor particles whose chromaticity coordinates fall within the range given above are less colored, making it

possible to avoid reduction of the emission efficiency and influences given to the color emission. Further, it is desirable for the spherical phosphor particles of the present invention to have a reflectance of at least 95%.

For forming the phosphor layer by using the particular spherical phosphor particles, a phosphor powder for each color is mixed in a binder solution consisting of, for example, polyvinyl alcohol, n-butyl alcohol, ethylene glycol and water so as to prepare a paste. Then, the resultant paste is coated by means of, for example, screen printing so as to form the desired phosphor layer.

It is desirable for the phosphor layer to have a uniform thickness. To be more specific, a difference in thickness of the phosphor layer between a point 20 μm apart from the upper edge of the rib and a central point of the address electrode should be at most 25%, preferably at most 20%. A phosphor layer meeting this requirement is considered to have a uniform thickness. A phosphor layer having a uniform thickness can be irradiated uniformly with ultraviolet rays. Where the phosphor layer has a large local difference in thickness, some phosphor particles are positioned behind other phosphor particles, resulting in failure to be irradiated with the ultraviolet rays. It should be noted that the spherical phosphor particles defined in the present invention are also advantageous in making the phosphor layer thickness uniform.

In order to permit the light emitted from the phosphor to be transmitted efficiently to the outside, it is effective to dispose a reflective layer of a visible light between the phosphor layer and the rear substrate and between the phosphor layer and the rib. For increasing the reflection of the emitted light, it is desirable to form a visible light reflective layer over substantially the entire region between the phosphor layer and each of the other members of the PDP including the rear substrate, the address electrode and the rib. The materials effectively reflecting the visible light, which can be used in the present invention, include, for example, particles of MgO, MgF_2, α-Al_2O_3, $MgAl_2O_4$, $3Al_2O_3.5SiO_2$ and $2MgO.2Al_2O_3.5SiO_2$. Particularly, MgO particles can be used as the materials effectively reflecting the visible light. It is desirable for these materials to have an average particle size of 10 to 200 nm. The particles having an average particle size falling within the range noted above permit effectively scattering the visible light. Also, these materials are satisfactory in the electron emitting characteristics, compared with TiO_2 used for forming a known white reflective layer. It follows that the materials used for forming the visible light reflective layer are also effective for facilitating the discharge. The visible light reflective layer should desirably have a thickness of 0.1 to 5 μm, preferably 0.1 to 1 μm. Where the thickness is less than 0.1 μm, the effect of reflecting the visible light cannot be obtained. Where the thickness exceeds 5 μm, however, the discharge space is diminished, leading to a low brightness.

FIG. **2** is a cross sectional view of a PDP showing that a visible light reflective layer **11** is formed to cover the rear substrate **2**, the address electrode **4** and the side surface of the rib **3**, and that the phosphor layer **5** is formed to cover the visible light reflective layer **11**.

If the phosphor layer **5** is formed by using spherical phosphor particles exhibiting a micro-resonator effect, the quantum efficiency which is said to be 30 to 80% in general can be improved in the present invention, leading to an improved brightness of the PDP. The term "micro-resonator effect" denotes a phenomenon which was observed first by Garrett et al. in CaF_2:Sm crystal sphere having a size of about 100 μm (C. G. Garrett et al., Phys. Rev. 124, 1807 (1961)). It is described in this literature that, if light is incident into the crystal sphere, total reflection of the light is repeated within the sphere to cause the light to be confined in the sphere, with the result that laser oscillation is brought about. The micro-resonator effect is also observed in other materials, e.g., polystyrene transparent microsphere having a size of about 40 μm and doped with Nile Red and fluoride glass sphere having a size of about 100 μm and doped with Nd^{3+}. Further, it is observed in an Eu chelate compound that a transition probability is increased by the micro-resonator effect so as to shorten the emission life time of Eu. However, observation of the micro-resonator effect has not yet been reported in the general crystalline rare earth phosphor.

FIGS. **4A** to **4C** are intended to explain the micro-resonator effect (i.e., the effect that microsphere cause light to exhibit Whispering Gallery Mode). Specifically, FIG. **4A** is a graph showing how the density of states of the light spontaneously emitted from the phosphor is dependent on the frequency. On the other hand, FIG. **4B** is a graph showing how the density of states of the light is dependent on the frequency when the light is confined three dimensionally to the space inside the microsphere of the phosphor. As is seen from FIG. **4B**, the light components having certain wavelengths are intensified. It should be noted in this connection that, when the light is confined within the microsphere as shown in FIG. **4C**, interference and resonance of the light take place within the sphere. When the wavelength of resonance is coincident with the wavelength of the light emitted from the phosphor, emitted is light having an intensity markedly higher than that of the spontaneously emitted light and also having a short life time.

In order to permit the light to be confined within the microsphere of phosphor, it is desirable for the spherical phosphor particles to have a particle size of 0.1 to 20 μm. Where the spherical phosphor particle has a particle size smaller than 0.1 μm, the micro-resonator effect is unlikely to take place. Further, where the phosphor is used in the manufacture of a PDP, the spherical phosphor particles are required to have a particle size falling within a range of between 0.1 μm and 5 μm. If the particle size exceeds 5 μm, the phosphor layer which is formed by coating tends to have an irregular surface.

The performance of the microresonator can be evaluated by Q-value, which is a factor denoting the loss. Specifically, the larger Q-value represents the smaller loss, and vice versa. For example, a Fabry-Perot resonator consisting of two plate mirrors has a Q-value of about 5,000. Also, a light resonator formed by fine processing of a semiconductor has a Q-value of about 100 to 5,000. It should be noted that the Q-value is dependent on the processing accuracy. When it comes to a resonator consisting of a microsphere, the accuracy of the sphere corresponds to the processing accuracy such that the microsphere which is theoretically spherical has a large Q-value. In other words, the resonator effect is increased where the surface of the spherical phosphor particle is free from irregularities or foreign substances which inhibit the passage of light.

To be more specific, a ratio of the maximum curvature to the minimum curvature of the phosphor particle should be at most 1.5 and should desirably be close to 1.0. The phosphor particle having a curvature ratio exceeding 1.5 indicates that edges or protrusions are present on the surface of the phosphor particle. In this case, it is impossible to obtain the micro-resonator effect. It is also desirable for the irregularities on the surface of the phosphor particle to be at most 5% of the particle diameter. FIG. **5** shows how to calculate the irregularities on the surface of the phosphor particle.

Specifically, a ratio of the irregularities is given by $(R'/R-1)\times 100$, where R denotes the diameter of the sphere covering the largest area of the phosphor particle, and R' represents the diameter of the sphere whose surface includes the tip of the largest projection on the surface of the phosphor particle. Further, the amount of the ultrafine particles attached to the surface of the phosphor particle should desirably be at most 0.01% by weight. The microresonator meeting these requirements has a Q-value of 1,000 to 100,000.

Where the phosphor powder is regarded as an aggregate of microspheres, the particle size distribution should desirably be sharp. Specifically, concerning the particle size distribution, each of the difference between 80% D value and 50% D value and the difference between 50% D value and 20% D value should desirably be at most 20%. For measuring the particle size distribution, the phosphor is dispersed in water. After stirred for at least 5 minutes, the particle size distribution is measured by a particle size distribution meter such as a microtrack. In this case, the particle size is measured on the basis of the number of particles. For example, "50%D" denotes the particle size where the accumulated value starting with the particle having the smallest particle size becomes 50%.

When it comes to a phosphor powder having the sharp particle size distribution as defined in the present invention, it is possible to obtain a uniform emission of a high brightness as a whole. On the other hand, where the phosphor powder has a broad particle size distribution, the effect of increasing the brightness is weakened.

For preparing the spherical phosphor particles exhibiting the microresonator effect, the raw material phosphor particles are melted within a heat plasma, followed by rapidly cooling the melt so as to obtain spherical phosphor particles. Then, the resultant spherical phosphor particles are dispersed in water or ethanol, and an ultrasonic wave is applied to the resultant dispersion. Further, a heat treatment is applied at a suitable temperature so as to prepare the desired spherical phosphor particles.

Since the spherical phosphor particle exhibiting a microresonator effect exhibits a high quantum efficiency, the thickness of the phosphor layer formed by using such phosphor particles can be decreased. The average thickness of the phosphor layer should desirably be at most 3 times the average particle size of the phosphor particles. FIG. **6** shows the phosphor layer **5** having a thickness about twice the average particle size of the phosphor particles **10**. Where the phosphor layer is formed thin, the discharge space can be enlarged, making it possible to increase the intensity of the vacuum ultraviolet rays emitted from the discharge gas.

It is also possible to form a reflective layer of ultraviolet rays between the phosphor layer and the rear substrate and between the phosphor layer and the rib. Of course, the reflective layer should consist of substances capable of reflecting the vacuum ultraviolet rays and visible light. In the case of forming an ultraviolet reflective layer, the phosphor is excited from both rearward and sideward so as to obtain emission efficiently. It follows that the ultraviolet reflective layer contributes to the improvement of the density of excited light required for bringing about the microresonator effect. The substances effective for reflecting the vacuum ultraviolet rays include, for example, fluorides such as MgF_2, LiF, CaF_2, and YF_3. The average particle size of the fluoride particle should desirably be about 0.5 to 1 μm. The fluoride particle meeting this requirement exhibits a high capability of emitting secondary electrons and also produces the effect of lowering the discharge voltage. Further, a thin film of a metal exhibiting a high reflectance in a VUV region such as Ir can be used as the ultraviolet reflective layer.

FIG. **3** is a cross sectional view showing a PDP prepared by forming an ultraviolet reflective layer **12** to cover the rear substrate **2**, the address electrode **4** and side surface of the rib **3**, followed by forming the phosphor layer **5** to cover the ultraviolet ray reflective layer **12**.

The microresonator effect described above can also be produced in phosphors other than those exemplified above and can also be utilized in displays other than the PDP. The phosphors adapted for producing the microresonator effect include, for example, crystals doped with a rare earth element or a transition metal element such as Al_2O_3:Cr, $BeAl_2O_4$:Cr, $InBO_3$:(Eu, Tb), (Y, Gd)BO_3:Eu, YAG:Nd, YF_3:Pr, $YGdF_4$:Pr, Y_2O_3:Eu, Y_2O_3:Pr, and Y_2O_3S:Eu. Phosphors doped with a rare earth element are suitable for use in a display.

These phosphors should also meet the requirements described previously. To reiterate, the average particle size should be 0.1 to 20 μm. Also, the irregularities on the surface of the phosphor particle should be at most 5% of the particle size. Further, the amount of the ultrafine particles attached to the surface of the phosphor particle should be at most 0.01% by weight. Still further, the phosphor particles should have a sharp particle size distribution such that each of the difference between the 80% D value and the 50% D value and the difference between the 50% D value and the 20% D value should be at most 20%.

EXAMPLES

Let us describe more in detail the present invention with reference to EXAMPLES which follow.

Comparative Example 1 and Examples 1a, 1b

An AC type PDP constructed as shown in FIG. **1** was prepared as follows. In the first step, prepared were a front substrate having transparent electrodes, bus electrodes, a transparent dielectric layer and a protective layer formed thereon and a rear substrate having address electrodes and ribs formed thereon.

For preparing a phosphor layer, each of the red-, green- and blue-emitting phosphor powders was mixed with a binder solution prepared by adding n-butyl alcohol and ethylene glycol to a 10% aqueous solution of polyvinyl alcohol having a saponification degree of 88% so as to prepare a phosphor paste. Then, predetermined cells of the rear substrate were coated with the resultant phosphor paste by screen printing method, followed by drying the coating to obtain a phosphor layer emitting red, green or blue light.

Further, the front substrate was disposed on the rear substrate having the phosphor layer formed thereon, followed by sealing the junction between the front and rear substrates. Finally, a mixed gas consisting of xenon, helium and neon was sealed in the discharge cell to establish a pressure of 500 Torr, thereby to prepare the desired PDP.

Comparative Example 1

Used were a red-emitting phosphor Y_2O_3:Eu, a green-emitting phosphor $BaAl_{12}O_{19}$:Mn and a blue-emitting phosphor $BaMgAl_{14}O_{23}$:Eu^{2+}, which were obtained by a flux method. Each of these phosphors was found to have an average particle size of 3 μm.

Example 1a

Each of the three kinds of the phosphor powders used in Comparative Example 1 was subjected to a treatment with a heat plasma. The resultant red-emitting phosphor Y_2O_3:Eu

was found to have an average particle size of 0.9 μm and an aspect ratio, i.e., a ratio of the longest diameter to the shortest diameter, of 1.05. Also, the resultant green-emitting phosphor $BaAl_{12}O_{19}$:Mn was found to have an average particle size of 1.2 μm and an aspect ratio of 1.10. Further, the resultant blue-emitting phosphor $BaMgAl_{14}O_{23}$:Eu^{2+} was found to have an average particle size of 1.0 μm and an aspect ratio of 1.10. A phosphor layer was formed by using each of these three kinds of the phosphors. The resultant phosphor layers were found to have a thickness of 20 μm at a point 20 μm apart from the tip of the rib and a thickness of 24 μm in the central point of the address electrode.

Example 1b

Before formation of the phosphor layer, a visible light reflective layer was formed as follows. Specifically, a paste was prepared by mixing MgO particles having an average particle size of 10 nm in the binder solution referred to previously. The surface of each cell of the rear substrate was coated with the resultant paste by screen printing method, followed by drying the coating, thereby to form a visible light reflective layer having a thickness of 1 μm. Then, predetermined cells of the rear substrate were coated with the three kinds of the phosphor pastes as in Example 1a, followed by drying the coating so as to form red-, green- and red-emitting phosphor layers.

The brightness of each color was measured in respect of the PDP prepared in each of Comparative Example 1, Example 1a and Example 1d, with the results as shown in Table 1 below:

TABLE 1

	Relative Brightness		
	R	G	B
Comparative Example 1	100	100	100
Example 1a	110	105	106
Example 1b	120	110	117

In Table 1, the brightness is given in terms of relative brightness with the brightness for Comparative Example 1 set at 100. As apparent from Table 1, the brightness was improved in each of Examples 1a and 1b, in which spherical phosphor particles were used, compared with Comparative Example 1. Further, the brightness in Example 1b, in which was formed a visible light reflective layer consisting of MgO fine particles, was found to be higher than that in Example 1a.

Comparative Example 2 and Examples 2a, 2b

A PDP was prepared as in Comparative Example 1 and Examples 1a, 1b reported above.

Comparative Example 2

Used were a red-emitting phosphor (Y, $Gd)_2O_3$:Eu, a green-emitting phosphor Zn_2SiO_5:Mn and a blue-emitting phosphor $BaMgAl_{14}O_{23}$:Eu^{2+}, which were obtained by a flux method. Each of these phosphors was found to have an average particle size of 2 μm. A phosphor layer was formed by using each of these three kinds of phosphors. The thickness of the phosphor layer was found to be nonuniform, i.e., 20 μm at a point 20 μm apart from the tip of the rib and 30 μm at a central point of the address electrode.

Example 2a

Each of the three kinds of the phosphor powders used in Comparative Example 2 was subjected to a treatment with a heat plasma to prepare spherical phosphor particles. The resultant phosphor powder was dispersed in water and subjected to washing with ultrasonic wave for 15 minutes, followed by drying. Further, the dried phosphor powder was subjected to a heat treatment at 1,000° C. for one hour.

FIG. **7** is an SEM photograph showing the red-emitting phosphor particle of (Y, $Gd)_2O_3$:Eu. As apparent from the photograph, irregularities were not found on the surface of the phosphor particle. Also, ultrafine particles were not found to be attached to the surface of the phosphor particle. Further, the phosphor particles were found to have an average particle size of 2 μm. The other phosphor particles were found to have similar shapes.

A phosphor layer was formed by using each of these three kinds of the phosphors. The resultant phosphor layer was found to have a thickness of 20 μm at a point 20 μm apart from the tip of the rib and a thickness of 22 μm in the central point of the address electrode.

Example 2b

Before formation of the phosphor layer, an ultraviolet reflective layer was formed as follows. Specifically, a paste was prepared by mixing MgF_2 particles having an average particle size of 1 μm in a binder solution. The surface of each cell of the rear substrate was coated with the resultant paste by screen printing method, followed by drying the coating, thereby to form an ultraviolet reflective layer having a thickness of 3 μm. Then, predetermined cells of the rear substrate were coated with the three kinds of the phosphor pastes as in Example 2a, followed by drying the coating so as to form red-, green- and red-emitting phosphor layers. The average thickness of each of the phosphor layers was set to be 6 μm.

The white brightness was measured in respect of the PDP prepared in each of Comparative Example 2, Example 2a and Example 2d, with the results as shown in Table 2 below:

TABLE 2

	White Brightness (Relative Value)
Comparative Example 2	100
Example 2a	120
Example 2b	150

In Table 2, the white brightness is given in terms of relative value with the white brightness for Comparative Example 2 set at 100. As apparent from Table 2, the white brightness was improved in each of Examples 2a and 2b, compared with Comparative Example 2. Particularly, a prominent improvement in brightness was achieved in Example 2b in which the phosphor layer was formed sufficiently thin so as to provide a larger discharge space. Further, a green afterimage, which was observed in each of Comparative Example 2 and Example 2a, was not observed in Example 2b.

Comparative Example 3 and Examples 3a, 3b

The brightness and emission life time of phosphor microspheres were measured by a method shown in FIG. **8**.

In the method shown in FIG. **8**, phosphor particles **10** are spread on a glass plate **21**. A photomultiplier **22** is arranged **10** cm above the phosphor particles. Further, a filter **23** is arranged in front of the photomultiplier **22**. On the other hand, an optical fiber **25** connected to a flash lamp **24** is

arranged below the glass plate **21** so as to irradiate the phosphor particles **10** with light. Further, the light emitted from the phosphor particles **10** is detected by the photomultiplier **22**, and a detection signal is converted into a voltage and is output on an oscilloscope **26**.

The brightness and emission life time of the phosphor microspheres were evaluated as follows. Specifically, the peak value of the signal output from the photomultiplier **22** was measured as the brightness. Also, an afterglow observed after stopping of the light irradiation was measured so as to determine as the emission life time the time required for the brightness of the afterglow to be lowered to a value which permits obtaining a signal value which is 10% of the peak value. Measurement was applied to, for example, 50 phosphor particles so as to obtain an average value.

Comparative Example 3

Particles of Al_2O_3 and Cr_2O_3, both available on the market, were weighed in a molar ratio of 1:0.1 and mixed for an hour in a ball mill. The resultant mixture was put in a crucible and baked at 1,300° C. for an hour within an electric furnace so as to prepare an Al_2O_3:Cr phosphor.

The resultant phosphor particles were found to be polyhedral. Concerning the particle size distribution, the phosphor particles were found to have a 50% D value of 4 μm, a 20% D value of 2 μm, and an 80% D value of 7 μm.

Example 3a

The Al_2O_3:Cr phosphor obtained in Comparative Example 3 was subjected to a heat plasma treatment under an argon atmosphere, a frequency of 14 MHz and a plate power of 5 kW. The powder taken out after the heat plasma treatment was dispersed in ethanol, and the dispersion was put in an ultrasonic wave washing device for application of an ultrasonic wave washing for 30 minutes. After the washing treatment, the powder was taken out of the washing device and, then, subjected to a heat treatment at 1,000° C. for an hour.

Irregularities or foreign substances were not recognized on the surfaces of the resultant phosphor particles. Also, the diameter of the resultant phosphor particle was constant regardless of the measuring point, which was 5 μm on the average, indicating that the phosphor particle was substantially spherical. Further, the amount of the ultrafine particles attached to the surface of the phosphor particle was found to be 0.001% by weight.

Example 3b

The Al_2O_3:Cr phosphor obtained in Example 3a was classified as follows. Specifically, 10 g of the phosphor powder was put in a beaker of 500 mL housing water. While stirring the powder-containing water with a stirrer, an ultrasonic wave was kept applied to the water for 30 minutes so as to disperse the powder particles. The resultant phosphor dispersion was quietly poured into a graduated measuring cylinder of 10L having water put therein in advance. After allowed to stand still for 30 minutes, the liquid present within a range of graduation lines 3L and 6L of the graduated measuring cylinder was sucked out with a rubber tube and, then, dried so as to obtain a phosphor powder.

Concerning the particle size distribution, the resultant phosphor powder was found to have a 50% D value of 5 μm, a 20% D value of 4.1 μm, and a 80% D value of 5.9 μm.

The brightness and the emission life time of the phosphor obtained in each of Comparative Example 3, Example 3a and Example 3b were measured by the methods described previously. Table 3 shows the results. In these measurement, used was a filter capable of transmitting light having wavelengths of 650 nm or more.

TABLE 3

	Brightness	Emission life time
Comparative Example 3	100	3 msec
Example 3a	400	100 μsec
Example 3b	300	300 μsec

In Table 3, the brightness is given in terms of relative brightness with the brightness for Comparative Example 3 set at 100.

As apparent from Table 3, the phosphor in each of Examples 3a and 3b was found to be superior to that in Comparative Example 3 in each of the brightness and the emission life time.

Comparative Example 4 and Example 4

The brightness and emission life time of the Y_2O_3:Eu phosphor were evaluated as in Comparative Example 3, Example 3a and Example 3b.

Comparative Example 4

Used was a Y_2O_3:Eu phosphor available on the market.

Example 4

A Y_2O_3:Eu phosphor available on the market was subjected to a heat plasma treatment under an argon gas atmosphere, a frequency of 5 MHz and a plate power of 20 kW. The powder taken out after the heat plasma treatment was dispersed in ethanol and, then, put in an ultrasonic wave washing device for washing of the powder with the ultrasonic wave for 30 minutes. After the washing treatment, the powder was subjected to a heat treatment at 1,000° C. for an hour.

Irregularities or foreign substances were not recognized on the surface of the resultant phosphor particle. Also, the diameter of the resultant phosphor particle was constant regardless of the measuring point, which was 4 μm on the average, indicating that the phosphor particle was substantially spherical. Further, the amount of the ultrafine particles attached to the surface of the phosphor particle was found to be 0.001% by weight.

The brightness and the emission life time of the phosphor obtained in each of Comparative Example 4, Example 4 were measured by the methods described previously. Table 4 shows the results. In these measurement, used was a filter capable of transmitting light having wavelengths of 590 nm or more.

TABLE 4

	Brightness	Emission life time
Comparative Example 4	100	1 msec
Example 4	200	300 μsec

In Table 4, the brightness is given in terms of relative brightness with the brightness for Comparative Example 4 set at 100.

As apparent from Table 4, the phosphor in Example 4 was found to be superior to that in Comparative Example 4 in each of the brightness and the emission life time.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalent.

We claim:

1. A plasma display panel, comprising:

a rear substrate provided with ribs defining discharge cells, address electrodes and phosphor layers; and

a front substrate provided with transparent electrodes extending in a direction perpendicular to the address electrodes, a transparent dielectric layer and a protective layer, discharge being brought about within the discharge cell formed between the rear substrate and the front substrate to excite the phosphor present in the phosphor layer, thereby causing the phosphor to emit a visible light,

wherein the phosphor particles forming the phosphor layer have an average particle size of 0.1–5 μm, an aspect ratio of 1.0–1.5 and a particle size distribution such that each of the differences between 80% D value and 50% D value and between 50% D value and 20% D value is at most 20%.

2. The plasma display panel according to claim 1, wherein a difference in thickness of said phosphor layer between a point 20 μm apart from an upper end of said rib and a central point of said address electrode is at most 25%.

3. The plasma display panel according to claim 1, wherein a reflective layer is formed between said phosphor layer and said rear substrate and between said phosphor layer and a side surface of said rib, said reflective layer comprising a substance selected from the group consisting of MgO, MgF_2, α-Al_2O_3, $MgAl_2O_4$, $3Al_2O_3.5SiO_2$ and $2MgO.2Al_2O_3.5SiO_2$.

4. The plasma display panel according to claim 3, wherein said substance has an average particle size of 10 to 200 nm.

5. A plasma display panel, comprising:

a rear substrate provided with ribs defining discharge cells, address electrodes and a phosphor layers; and

a front substrate provided with transparent electrodes extending in a direction perpendicular to the address electrodes, a transparent dielectric layer and a protective layer, discharge being brought about within the discharge cell formed between the rear substrate and the front substrate to excite the phosphor contained in the phosphor layer so as to cause the phosphor to emit a visible light,

wherein the phosphor particles forming the phosphor layer have an average particle size of 0.1 to 5 μm and a ratio of the largest curvature to the smallest curvature of at most 1.5.

6. The plasma display panel according to claim 5, wherein the magnitude of the irregularities on the surface of said phosphor particle is at most 5% of the particle diameter of the phosphor particle.

7. The plasma display panel according to claim 5, wherein the amount of ultrafine particles attached to the surface of said phosphor particle is at most 0.01% by weight.

8. The plasma display panel according to claim 5, wherein an average thickness of said phosphor layer is greater than an average particle size of said phosphor particles and less than three times as large as the average particle size of said phosphor particles.

9. The plasma display panel according to claim 6, wherein a reflective layer is formed between said phosphor layer and said rear substrate and between said phosphor layer and a side surface of said rib, said reflective layer comprising a substance selected from the group consisting of MgF_2, LiF, CaF_2, YF_3 and Ir.

* * * * *

US005921836A

United States Patent [19]

Nanto et al.

[11] **Patent Number: 5,921,836**

[45] **Date of Patent: Jul. 13, 1999**

[54] **APPARATUS FOR FORMING FLUORESCENT LAYERS OF A PLASMA DISPLAY PANEL AND METHOD THEREFOR**

[75] Inventors: **Toshiyuki Nanto**; **Teruo Kurai**; **Masayuki Wakitani**, all of Kawasaki; **Ryouichi Miura**; **Yasuo Yanagibashi**, both of Satsuma-gun, all of Japan

[73] Assignee: **Fujitsu Limited**, Kawasaki, Japan

[21] Appl. No.: **08/789,667**

[22] Filed: **Jan. 27, 1997**

[30] **Foreign Application Priority Data**

May 9, 1996	[JP]	Japan	8-114884
Dec. 17, 1996	[JP]	Japan	8-337189

[51] **Int. Cl.**[6] **H01J 1/30**

[52] **U.S. Cl.** **445/24**; 445/58; 445/60

[58] **Field of Search** 445/24, 52, 58, 445/60

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,916,012	12/1959	Hergenrother et al. .	
4,267,204	5/1981	Tomita et al. .	
5,601,468	2/1997	Fujii et al.	445/24
5,643,034	7/1997	Mohri et al.	445/24

FOREIGN PATENT DOCUMENTS

55-32314	3/1980	Japan .
57-21223	5/1982	Japan .
57-084545	8/1982	Japan .
61-245106	10/1986	Japan .
63-155527	11/1988	Japan .
5-299019	11/1993	Japan .
7-021913	1/1995	Japan .

Primary Examiner—Kenneth J. Ramsey
Attorney, Agent, or Firm—Staas & Halsey

[57] **ABSTRACT**

There is disclosed an apparatus for forming a fluorescent layer in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate. The apparatus includes: a platform for mounting the substrate thereon; a dispenser having at least one nozzle for ejecting the fluorescent paste; a transporter for moving the nozzle relative to the platform; and a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into the predetermined grooves between the ribs.

26 Claims, 17 Drawing Sheets

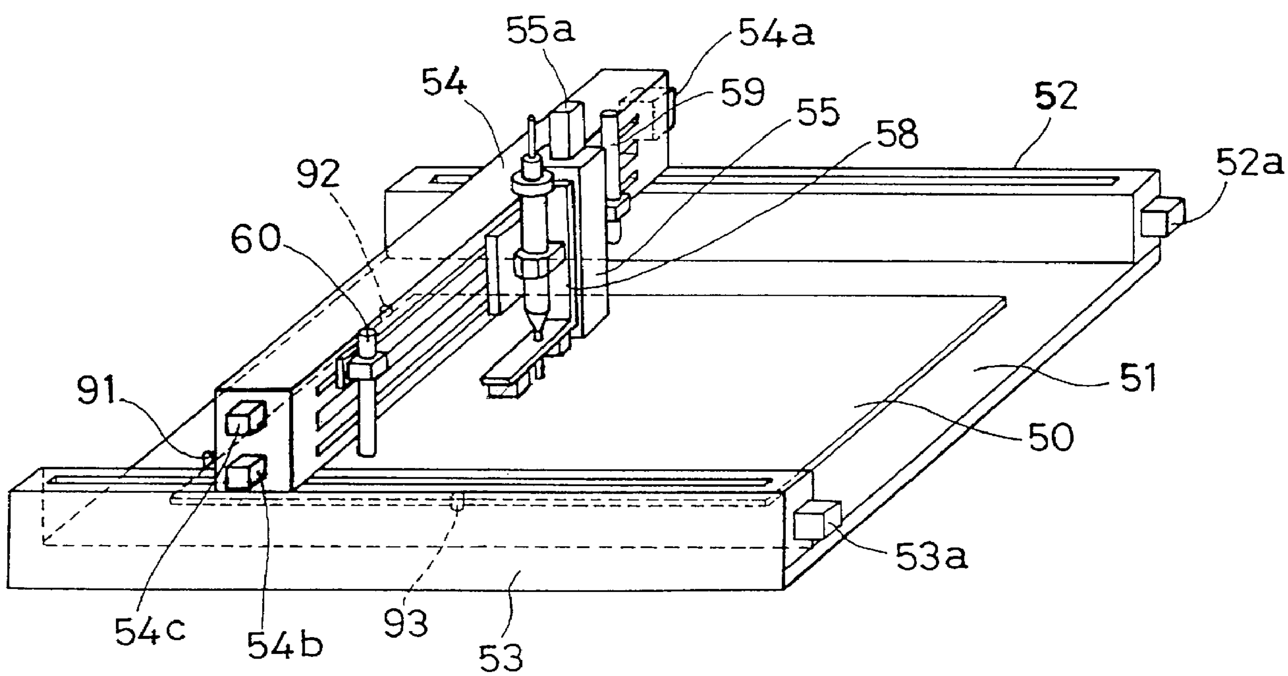


Fig.1

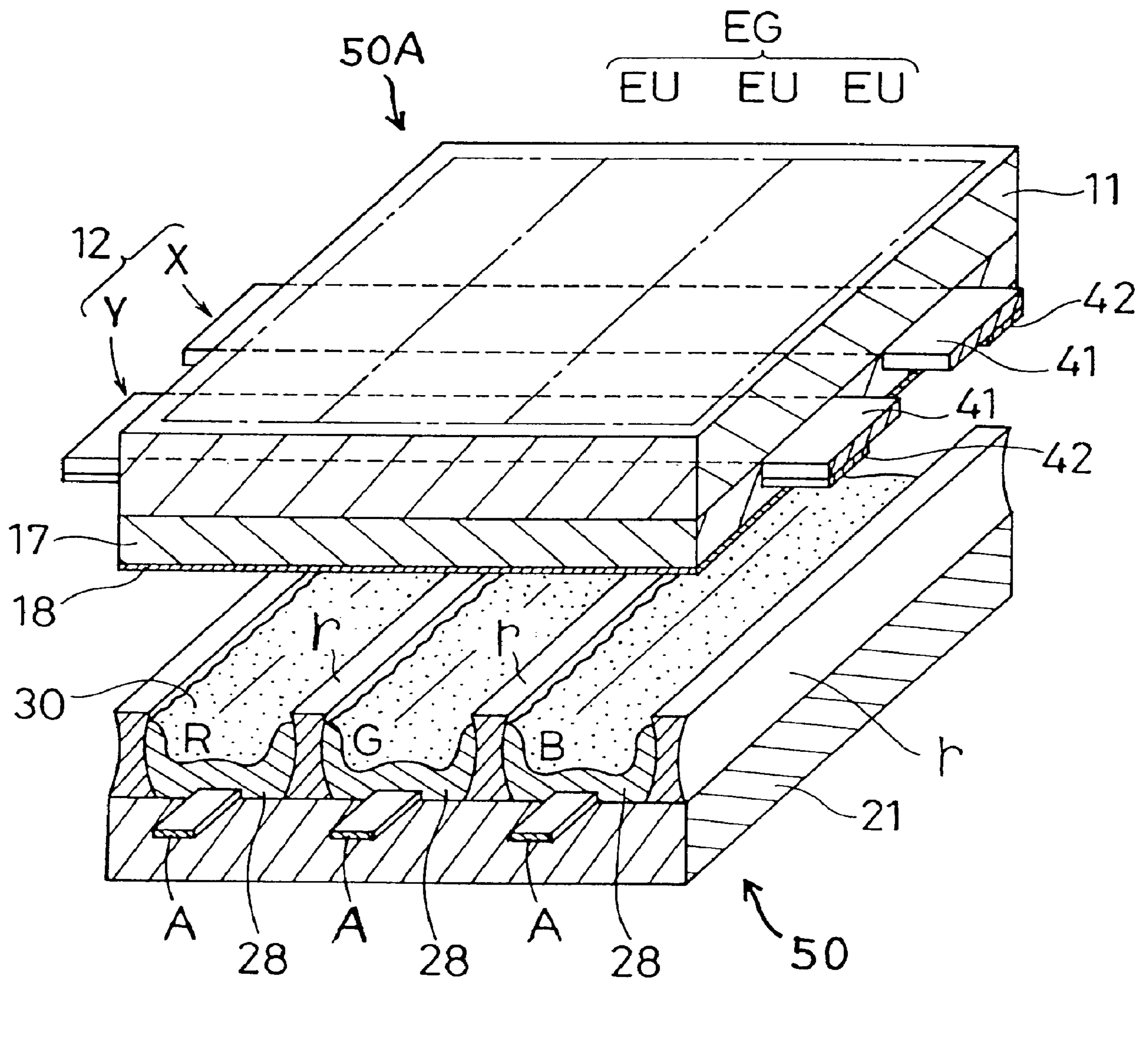

50A
EG
EU
EU
EU
11
12
X
Y
42
41
41
42
17
18
30
r
r
R
G
B
r
21
A
A
A
28
28
28
50

Fig.2

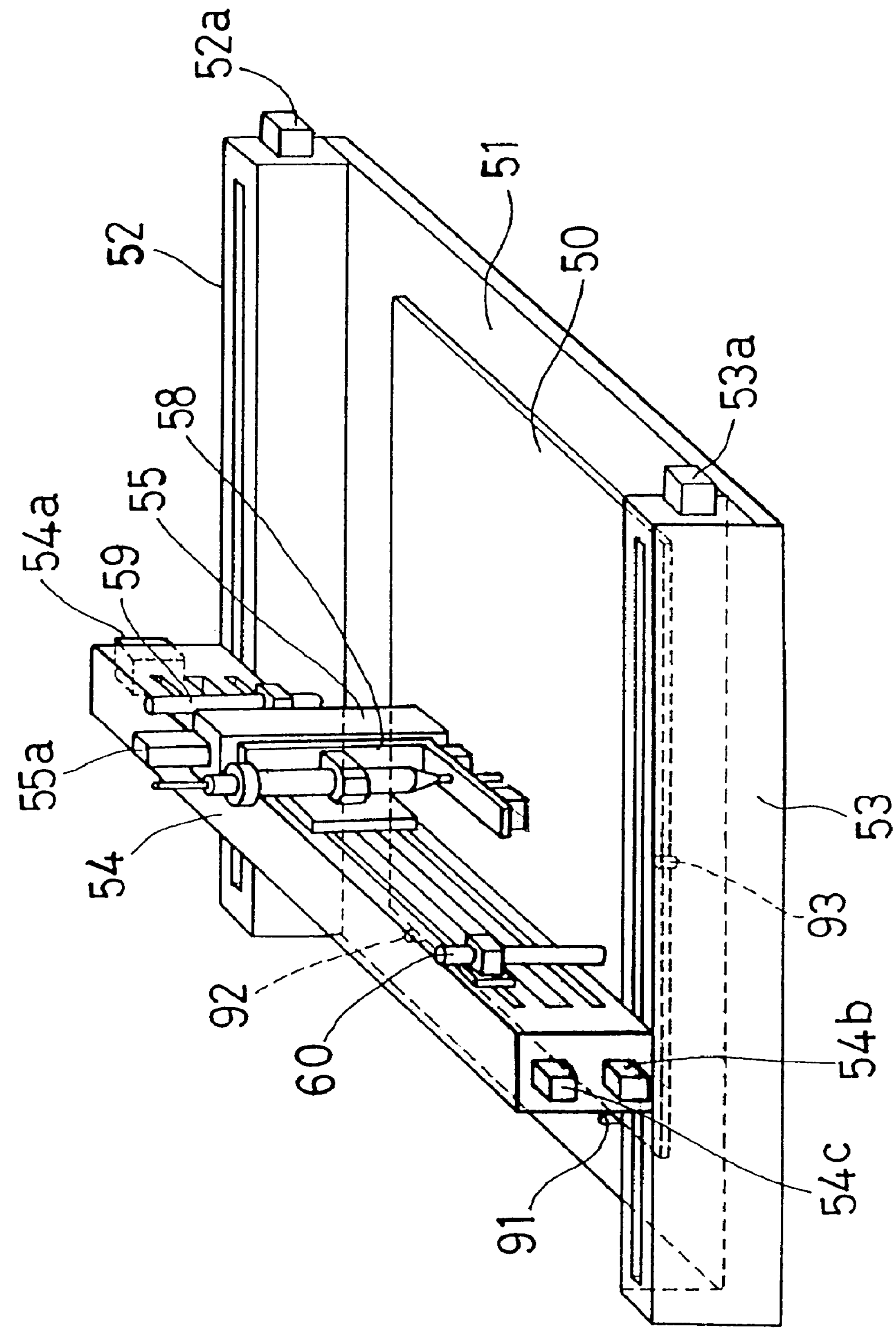


Fig.3

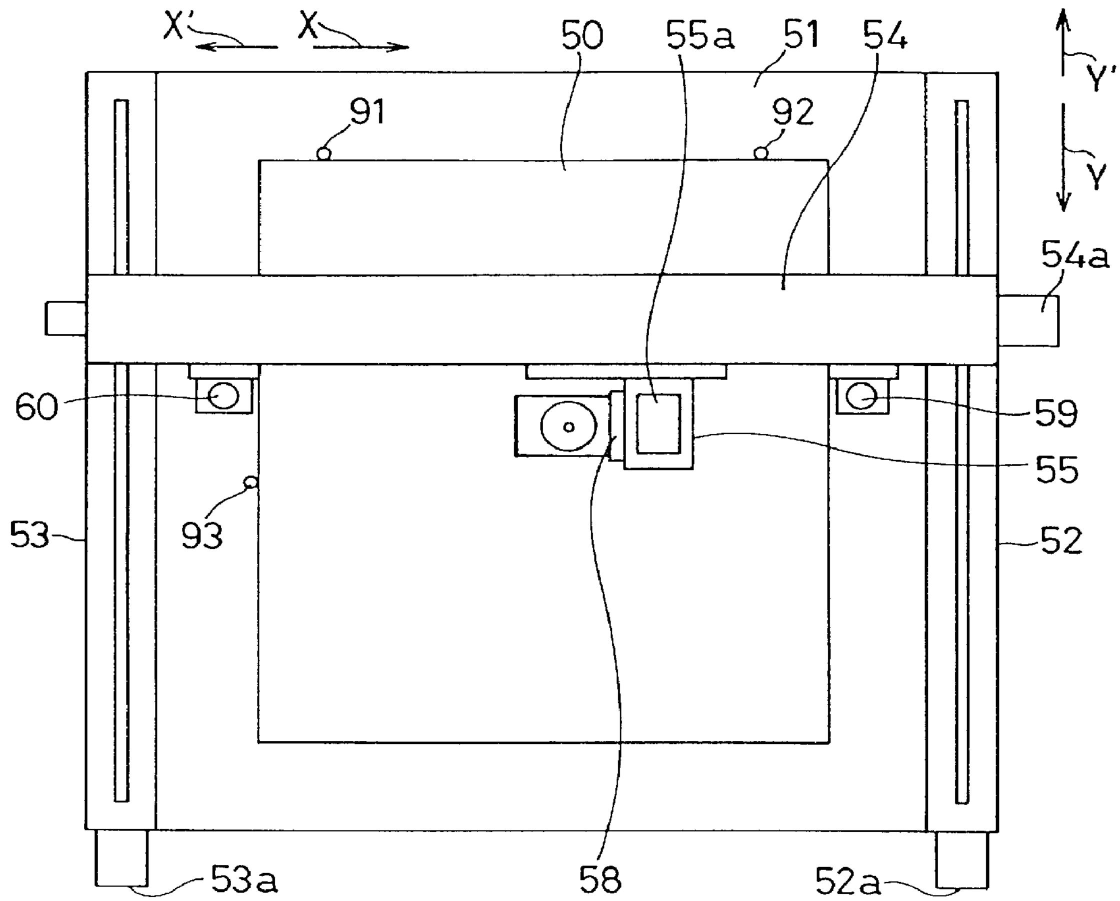

X'
X
50
55a
51
54
Y'
Y
91
92
54a
60
59
55
53
93
52
53a
58
52a

Fig.4

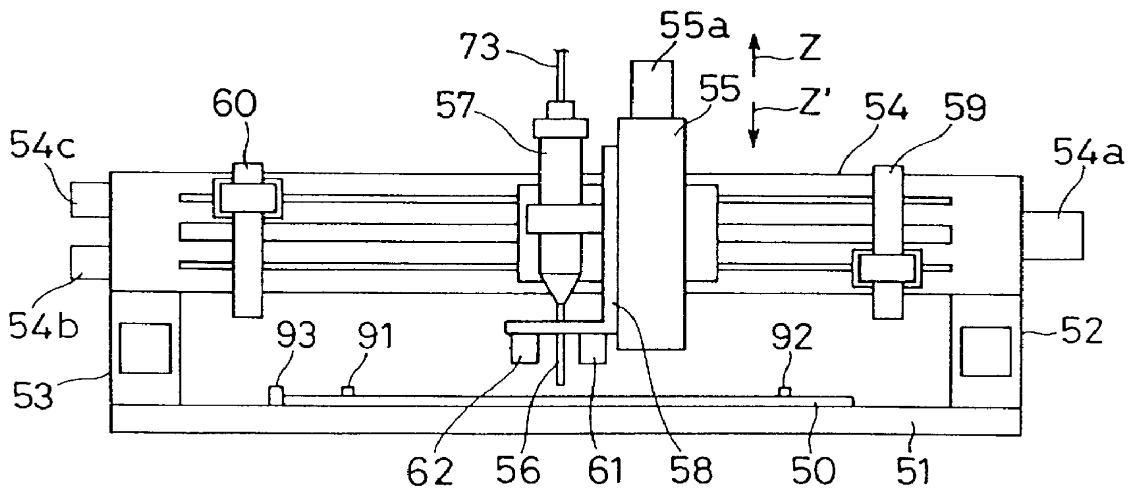

55a
73
Z
55
Z'
57
60
54
59
54c
54a
54b
93
91
92
52
53
62
56
61
58
50
51

Fig.5

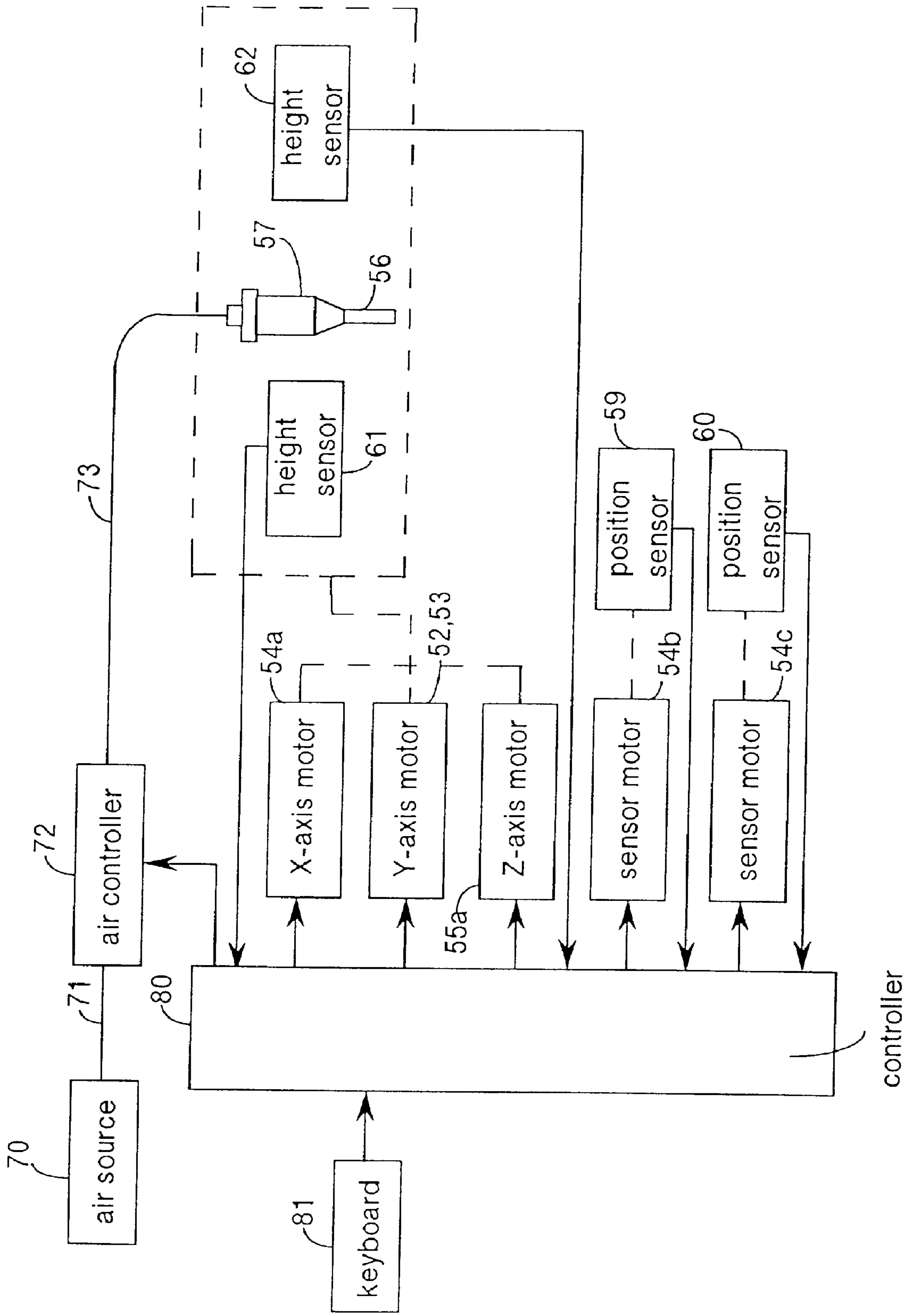

62
height sensor
57
56
height sensor
61
73
position sensor
59
position sensor
60
52,53
54a
54b
54c
X-axis motor
Y-axis motor
Z-axis motor
sensor motor
sensor motor
55a
72
air controller
71
80
controller
70
air source
81
keyboard

Fig.6

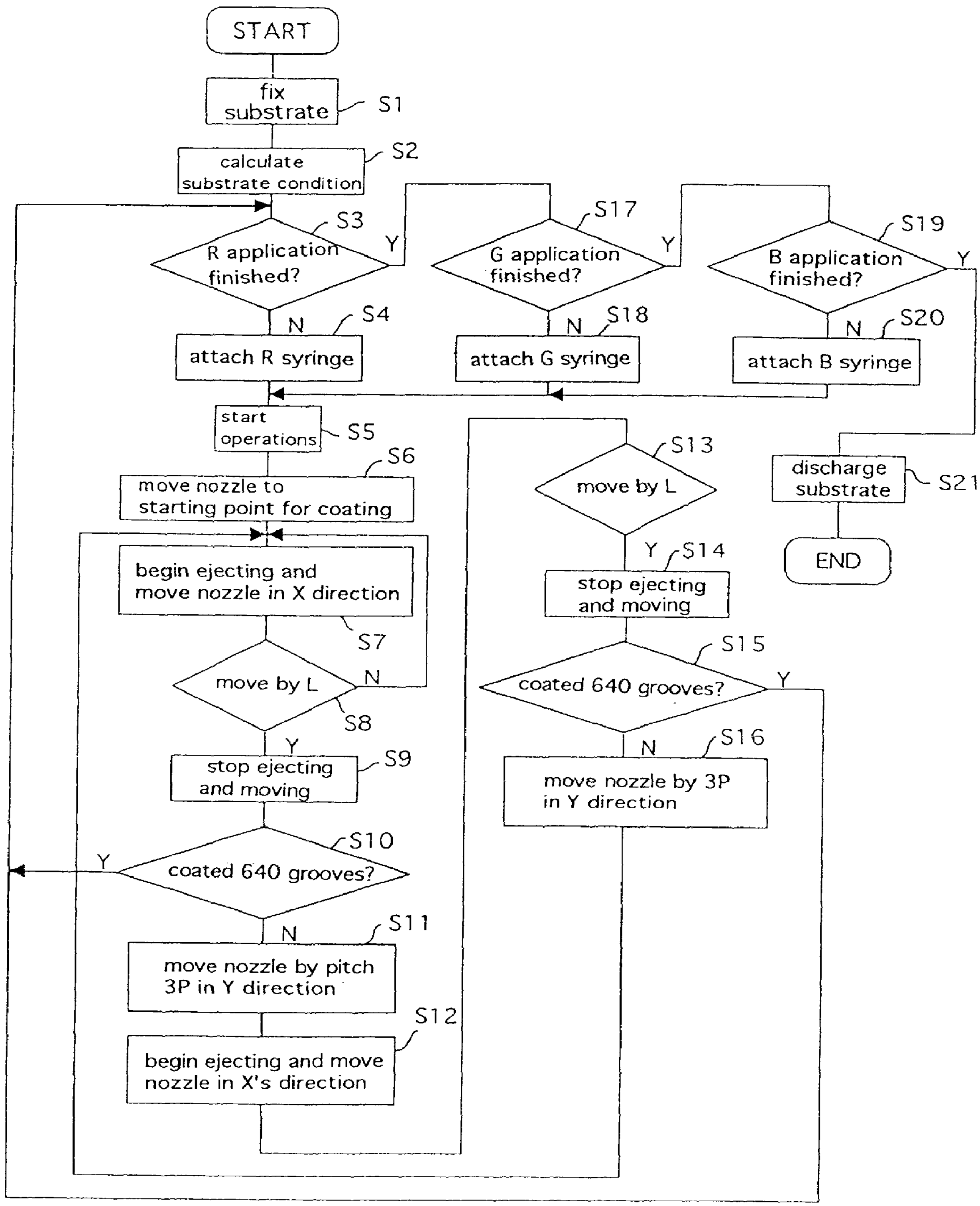

START
fix substrate
S1
calculate substrate condition
S2
R application finished?
S3
Y
N
attach R syringe
S4
G application finished?
S17
Y
N
attach G syringe
S18
B application finished?
S19
Y
N
attach B syringe
S20
start operations
S5
move nozzle to starting point for coating
S6
begin ejecting and move nozzle in X direction
S7
move by L
S8
N
Y
stop ejecting and moving
S9
coated 640 grooves?
S10
Y
N
move nozzle by pitch 3P in Y direction
S11
begin ejecting and move nozzle in X's direction
S12
move by L
S13
Y
stop ejecting and moving
S14
coated 640 grooves?
S15
Y
N
move nozzle by 3P in Y direction
S16
discharge substrate
S21
END

Fig.7

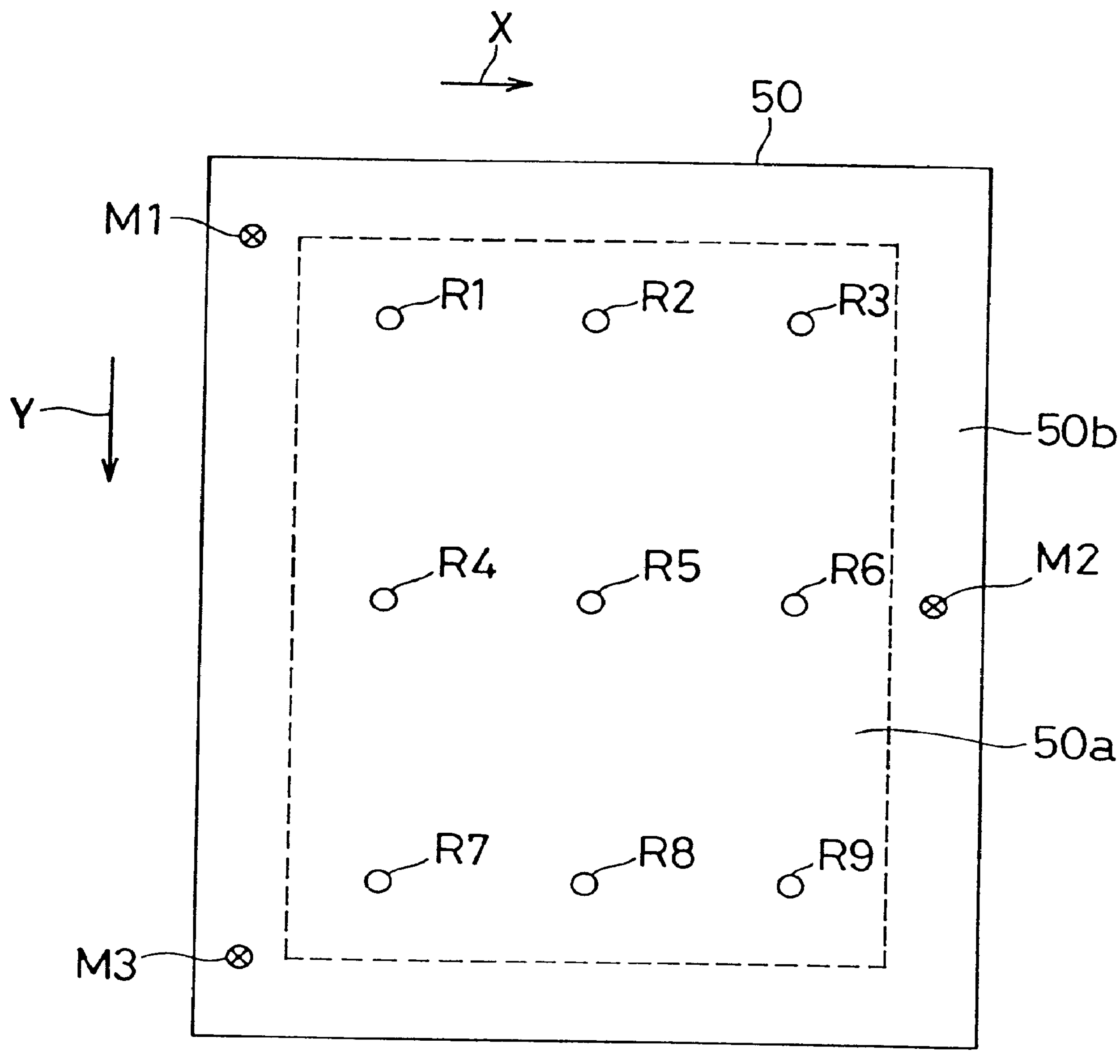


Fig.8

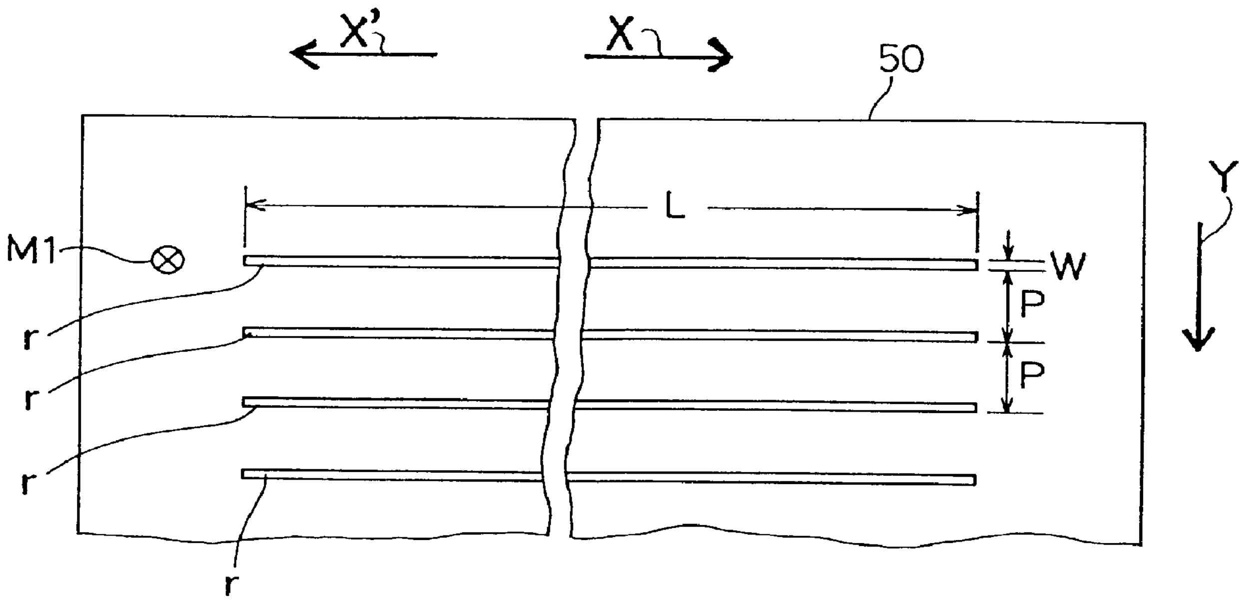


Fig.9

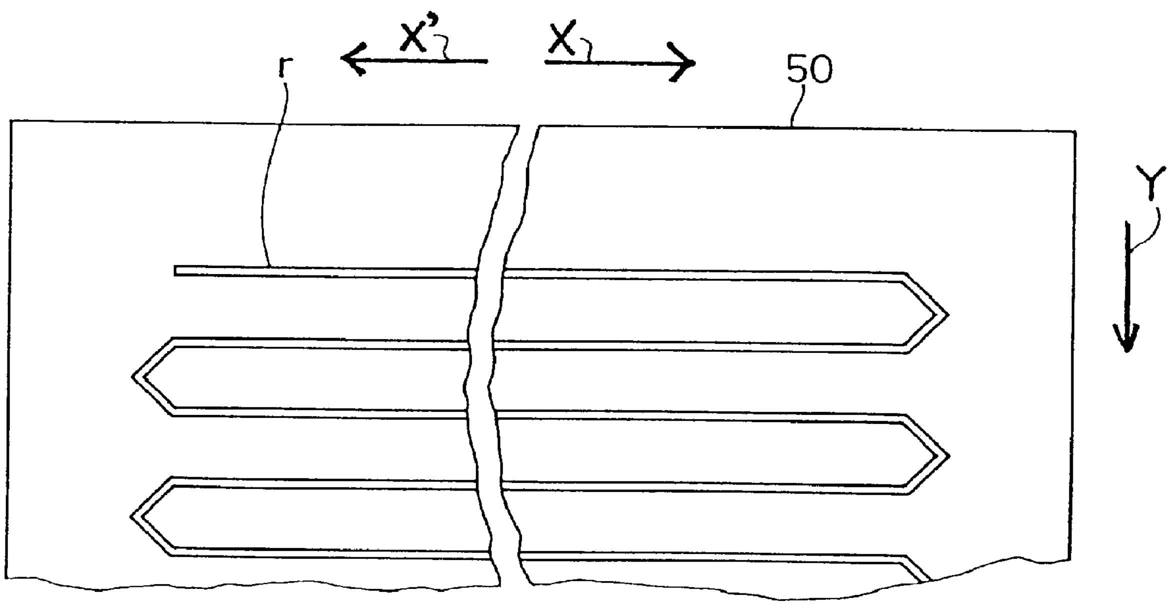


Fig.10

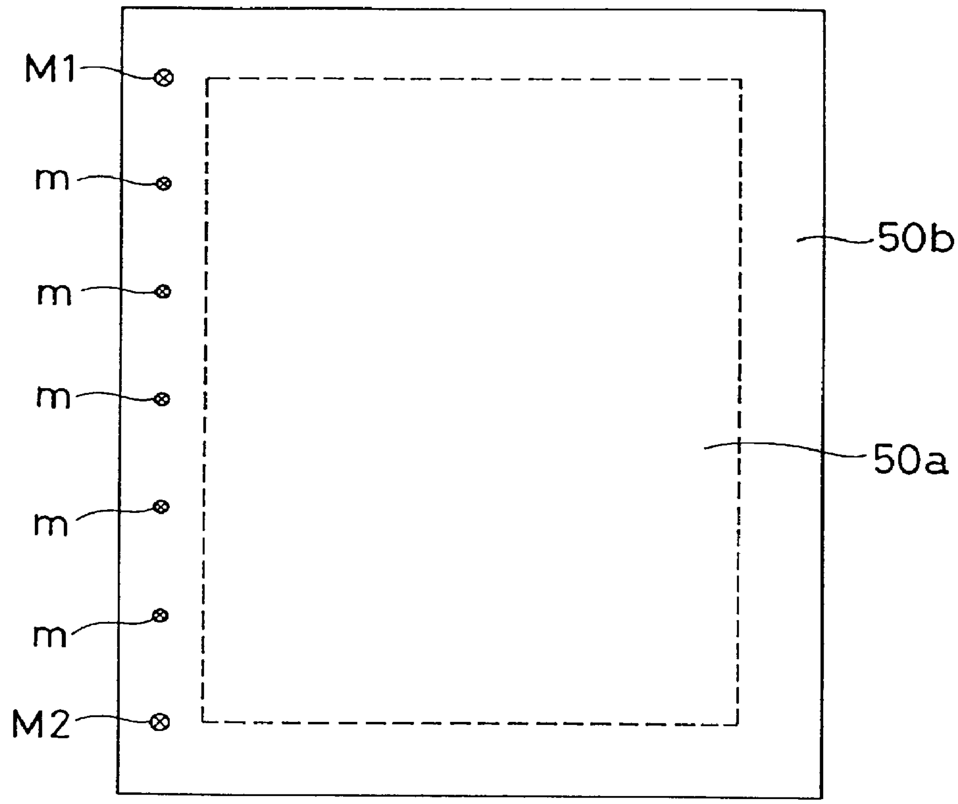


Fig.11

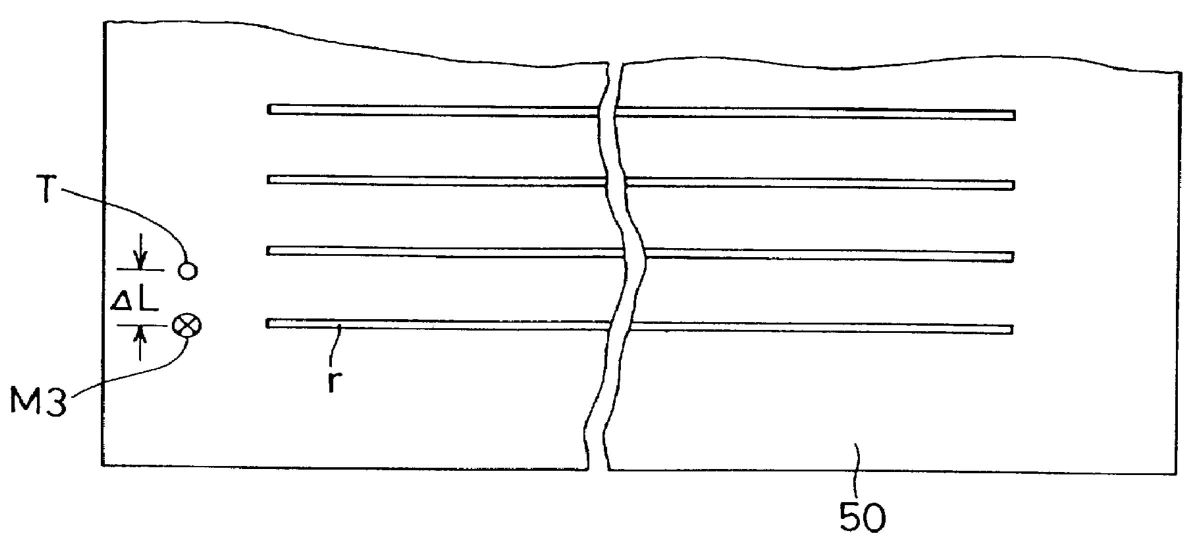


Fig.12

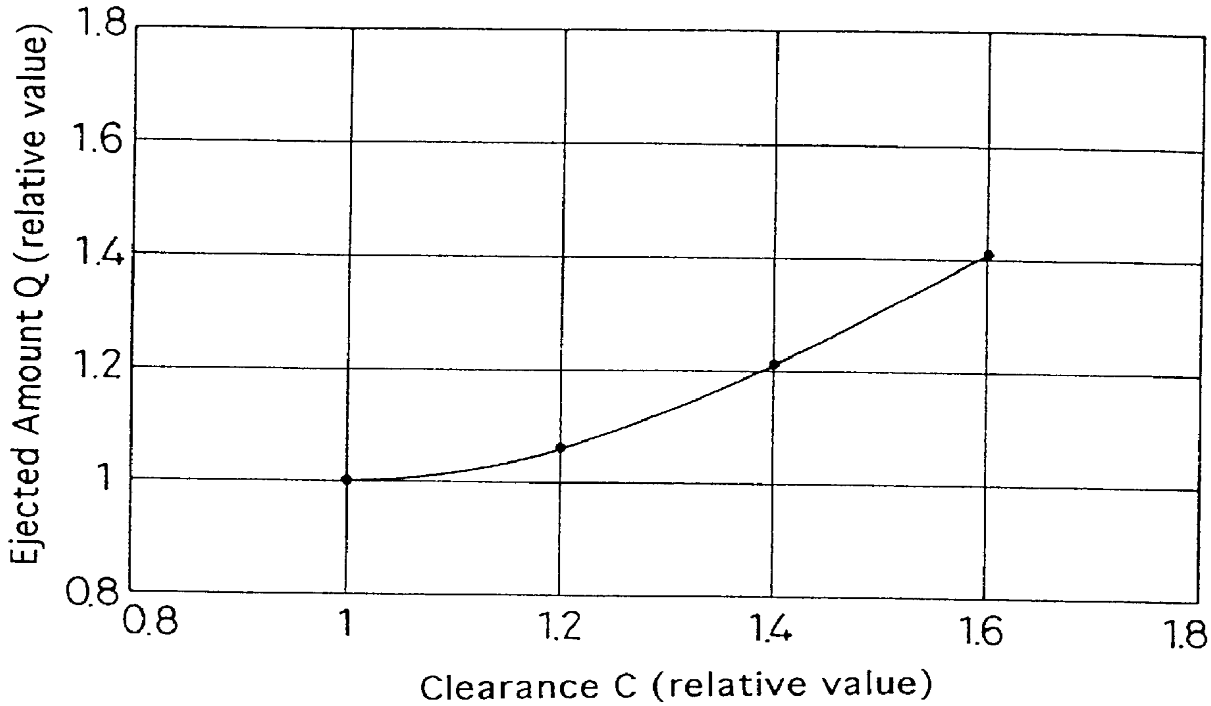

1.8
1.6
1.4
1.2
1
0.8
Ejected Amount Q (relative value)
0.8
1
1.2
1.4
1.6
1.8
Clearance C (relative value)

Fig.13

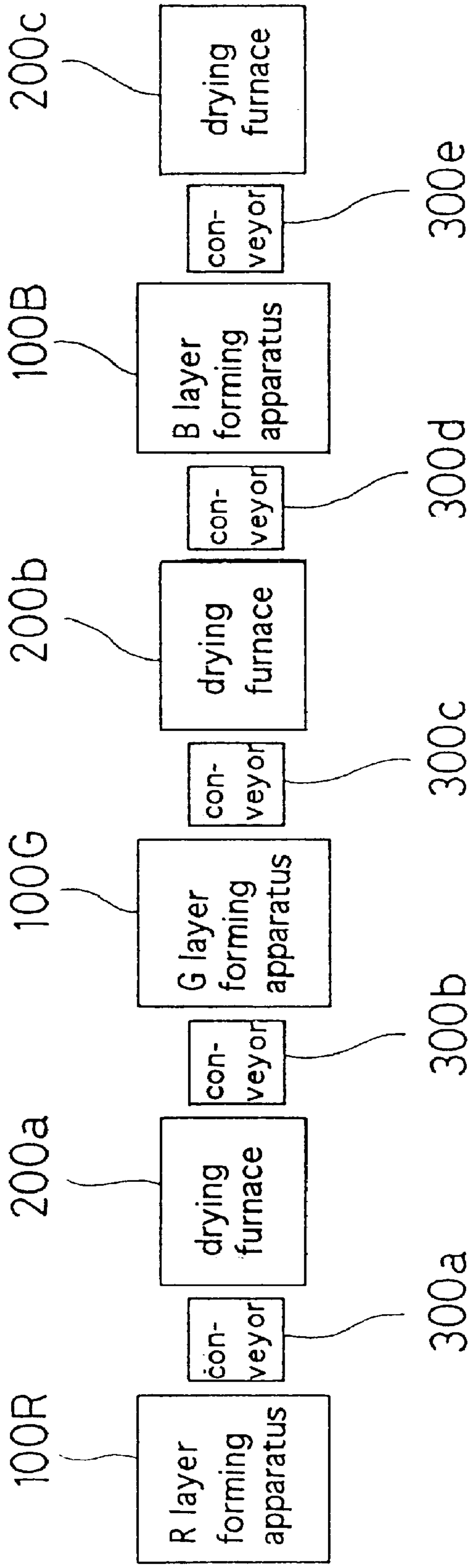

100R
R layer forming apparatus
con- veyor
300a
200a
drying furnace
con- veyor
300b
100G
G layer forming apparatus
con- veyor
300c
200b
drying furnace
con- veyor
300d
100B
B layer forming apparatus
con- veyor
300e
200c
drying furnace

Fig.14

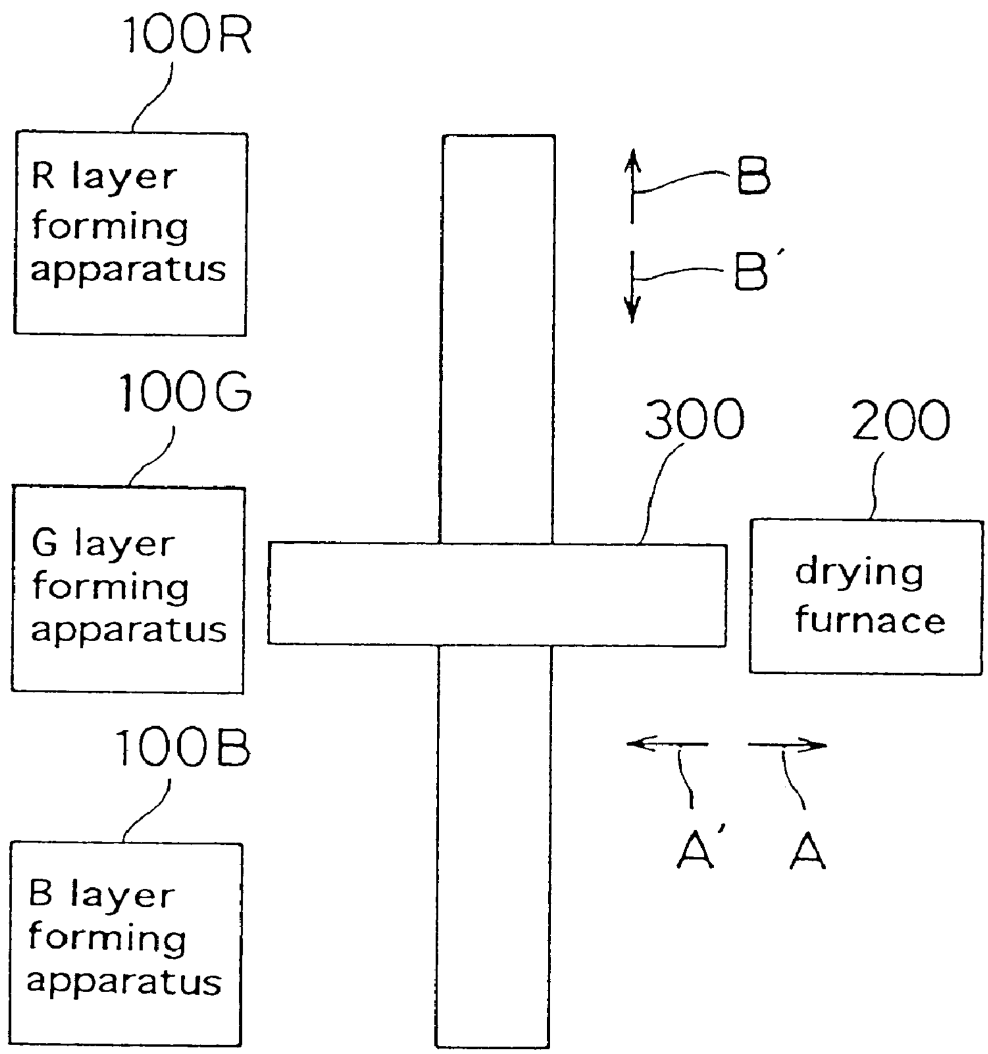

100R
R layer forming apparatus
100G
G layer forming apparatus
100B
B layer forming apparatus
B
B'
300
200
drying furnace
A'
A

Fig.15

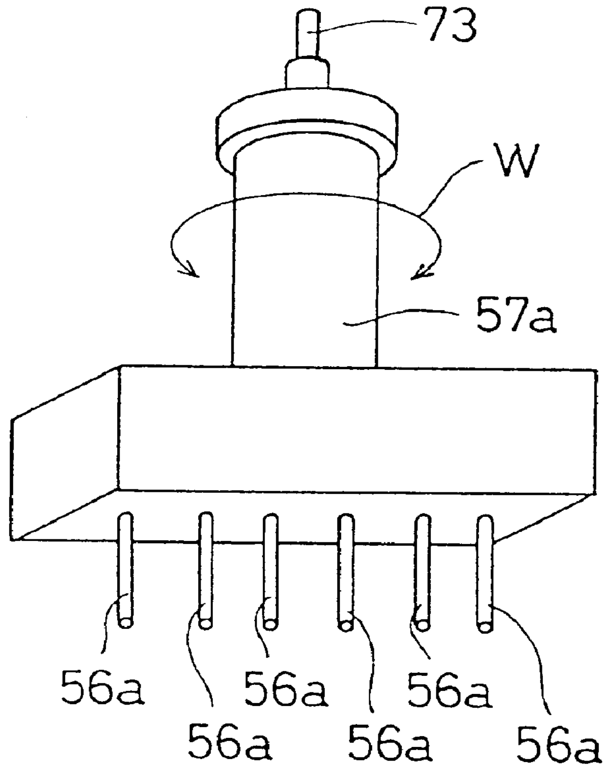


Fig.16

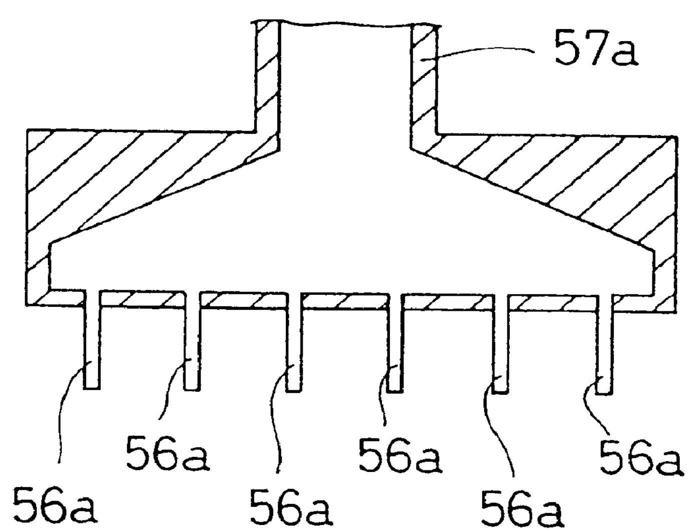


Fig.17

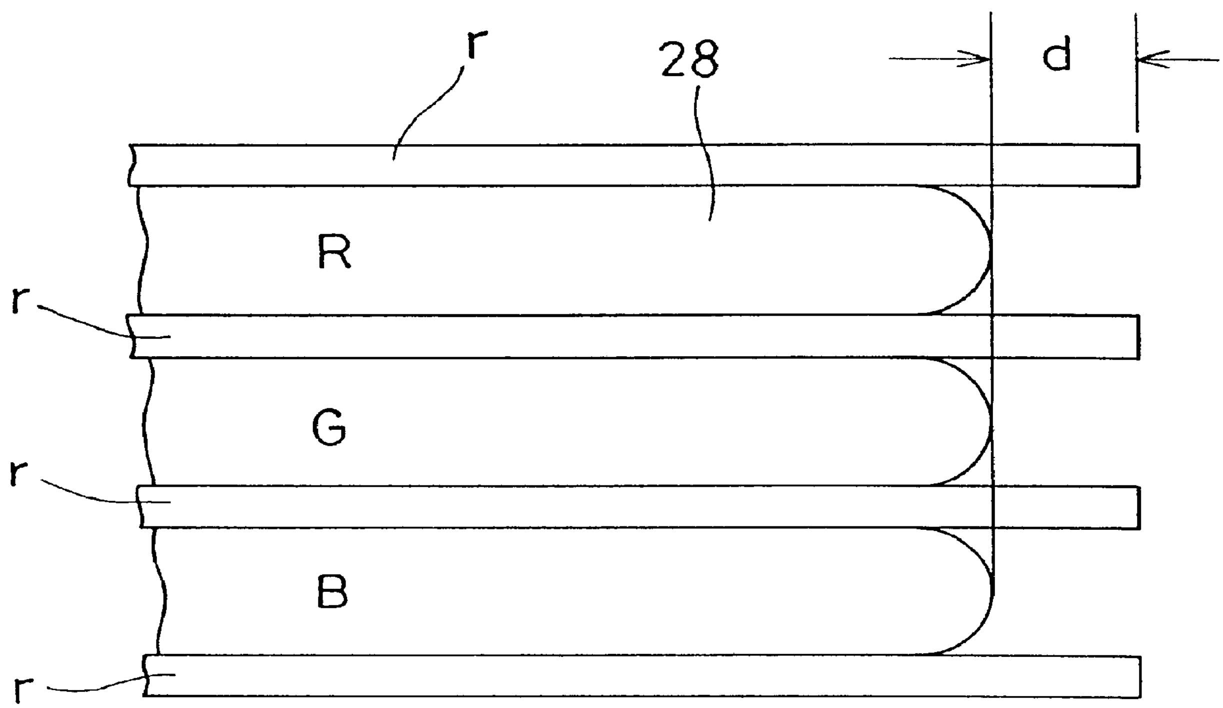


Fig.18

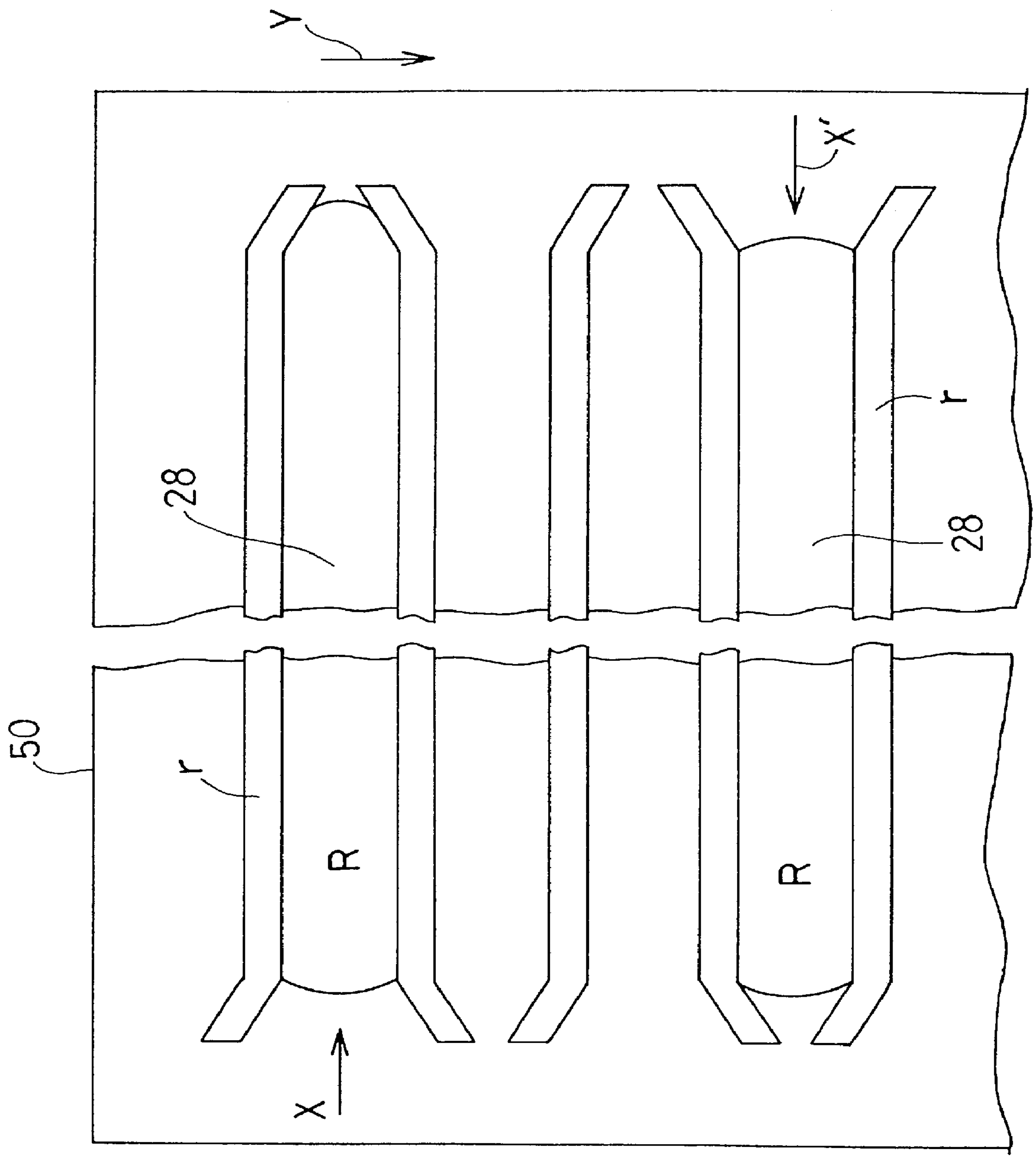


Fig.19

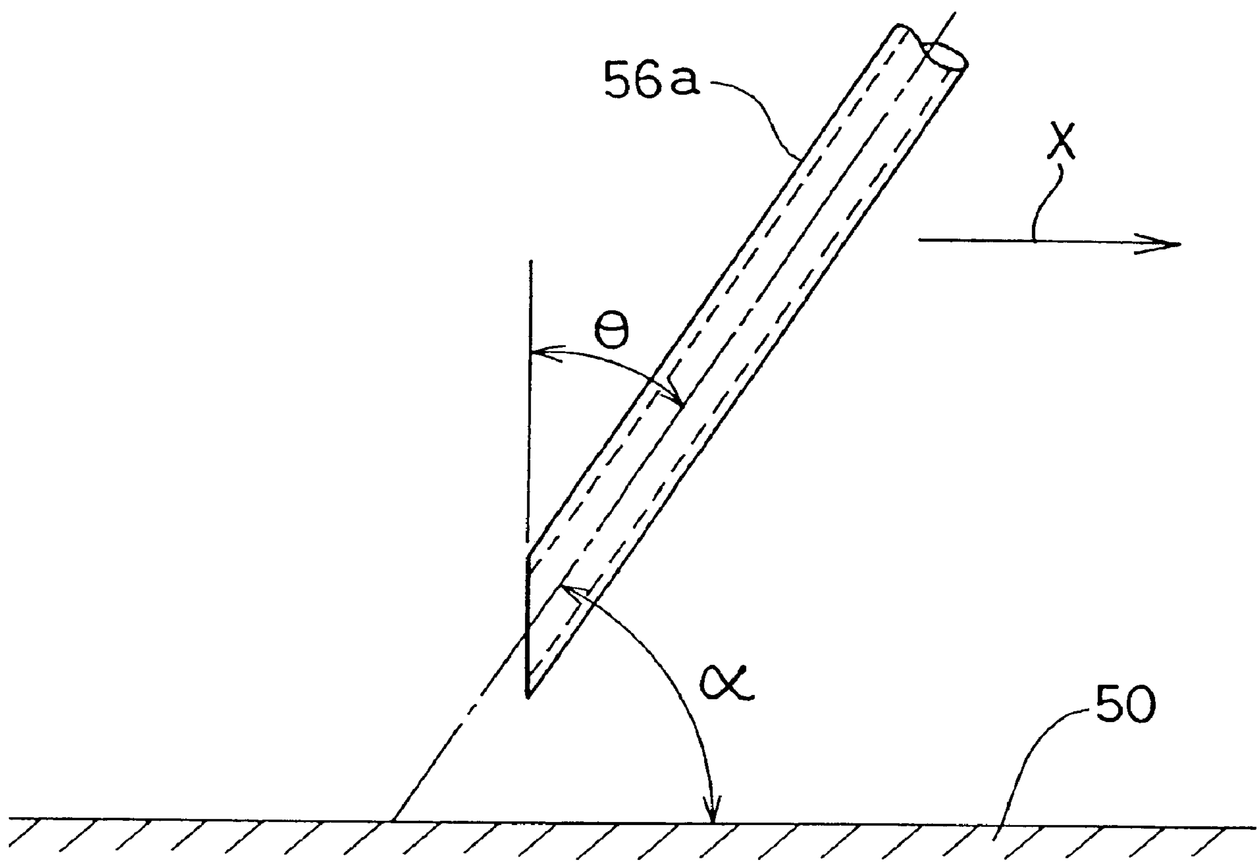


Fig.20

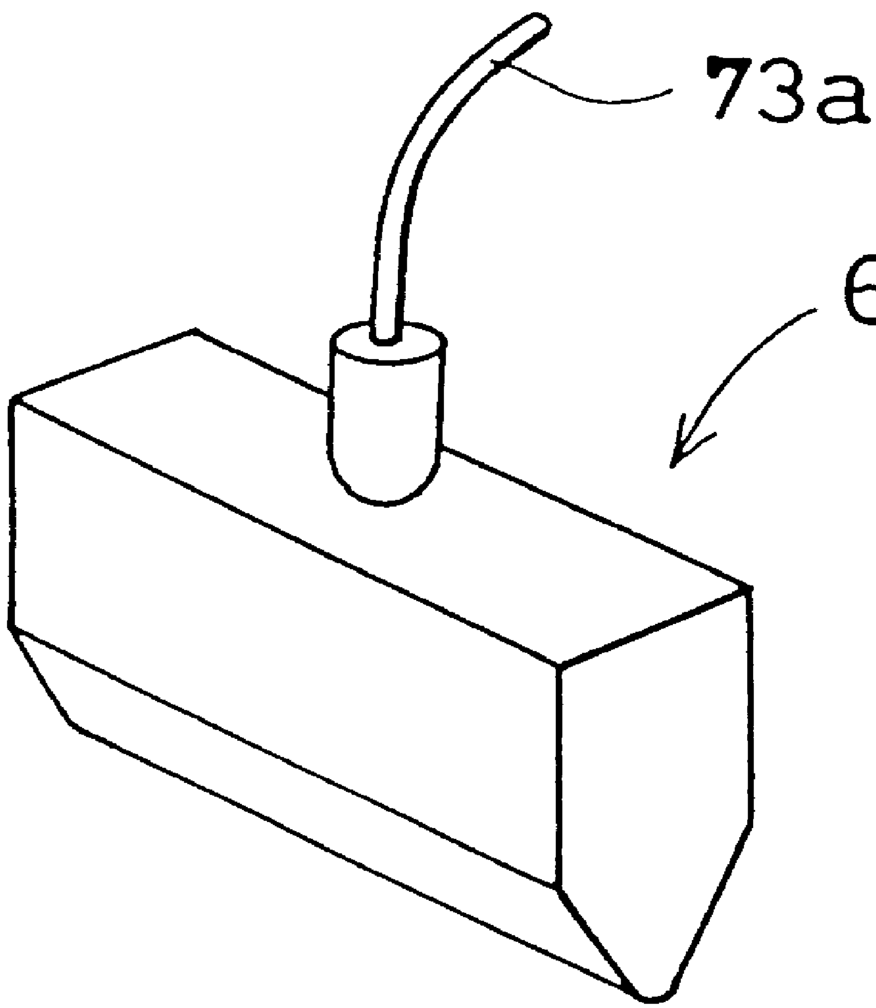


Fig.21

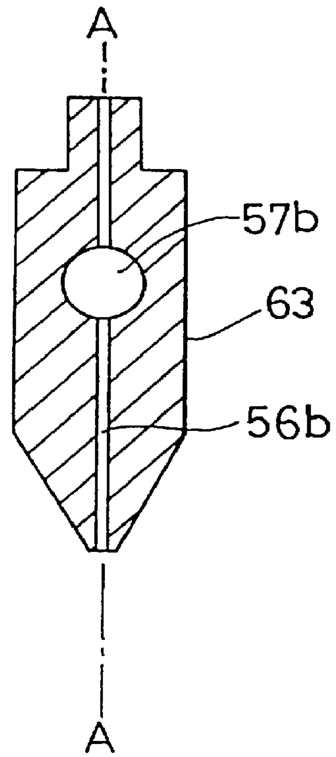
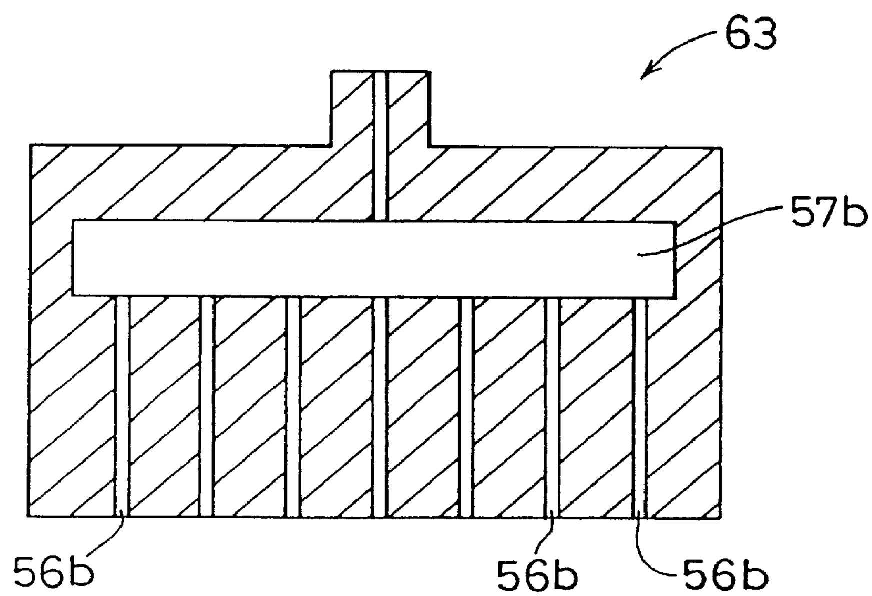


Fig.22



APPARATUS FOR FORMING FLUORESCENT LAYERS OF A PLASMA DISPLAY PANEL AND METHOD THEREFOR

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an apparatus for forming fluorescent layers of a plasma display panel and a method therefor. More particularly, the present invention relates to an apparatus which is used in manufacturing a plasma display panel (PDP) and which forms, on a substrate having a plurality of ribs (partition walls) on the surface thereof, a fluorescent layer in each of the spaces formed between the ribs and a method therefor.

2. Description of the Related Arts

A PDP is a display panel having, as a base, a pair of substrates (typically, glass plates) disposed opposite to each other with a discharge space sandwiched therebetween. In a PDP, by disposing a fluorescent layer of an ultraviolet-ray excitation type in the discharge space, it is possible to display a color since the fluorescent layer is excited by electric discharge. PDPs for displaying colors have three fluorescent layers of R (red), G (Green), and B (Blue).

Conventionally, fluorescent layers of R, G, and B were manufactured by successively applying, on a substrate, fluorescent pastes for the three colors containing powder-like fluorescent particles as a major component by screen printing method, followed by drying and sintering (for example, see Japanese Unexamined (Kokai) Patent Publication No. Hei 5(1993)-299019).

However, as the screen size of PDPs increase, an alignment shift is brought about between a positioning pattern and a mask pattern of the ribs due to the expansion and contraction of the screen mask, an error in positioning, and the like, so that it is becoming more and more difficult to achieve precise application of the fluorescent pastes between the ribs.

SUMMARY OF THE INVENTION

The present invention has been made in view of the above circumstances and the purpose thereof is to provide an apparatus for forming fluorescent layers uniformly and precisely between the ribs on the substrate for constructing a large PDP, and a method therefor.

The present invention provides an apparatus for forming a fluorescent layer in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising: a platform for mounting the substrate thereon; a dispenser having at least one nozzle for ejecting the fluorescent paste; a transporter for moving the nozzle relative to the platform; and a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into the predetermined grooves between the ribs.

The present invention also provides a method for consecutively applying a plurality of fluorescent pastes having different colors into grooves formed between a plurality of ribs disposed in parallel on a substrate surface, the different colors including at least first and second colors, the method comprising the steps of: preparing a plurality of fluorescent layer forming apparatus each ejecting a fluorescent paste of each color; applying the fluorescent paste of the first color into first grooves on the substrate surface with one of the fluorescent layer forming apparatus, the first grooves corresponding to the fluorescent paste of the first color; drying the fluorescent paste of the first color applied into the first grooves to such a degree that at least no surface tension is generated; applying the fluorescent paste of the second color subsequently with another of the fluorescent layer forming apparatus into second grooves adjacent the first grooves on the substrate, the second grooves corresponding to the fluorescent paste of the second color; and drying the fluorescent paste of the second color applied into the second grooves to such a degree that at least no surface tension is generated, and alternately repeating the steps of applying and drying the fluorescent paste of each color.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a perspective view showing the essential part of a plasma display panel according to the present invention.

FIG. **2** is a perspective view showing an apparatus according to an embodiment of the present invention.

FIG. **3** is a plan view showing the apparatus according to the embodiment of the present invention.

FIG. **4** is a front view showing the apparatus according to the embodiment of the present invention.

FIG. **5** is a block diagram showing a controller according to the embodiment of the present invention.

FIG. **6** is a flow chart showing operations according to the embodiment of the present invention.

FIG. **7** is a top view showing a substrate according to the embodiment of the present invention.

FIG. **8** is an enlarged view showing the essential part of FIG. **7**.

FIG. **9** is an enlarged view showing the essential part of a modified substrate applied to the present invention.

FIG. **10** is a top view showing a modified substrate applied to the present invention.

FIG. **11** is an enlarged view showing another method for correcting the rib pitch on the substrate of FIG. **7**.

FIG. **12** is a graph showing the relationship between the clearance and the ejected amount of the fluorescent paste according to the present invention.

FIG. **13** is an explanatory view showing a construction of a system according to the present invention.

FIG. **14** is an explanatory view showing a construction of another system according to the present invention.

FIG. **15** is a perspective view showing a modified nozzle according to an embodiment of the present invention.

FIG. **16** is a cross-sectional view of the nozzle shown in FIG. **15**.

FIG. **17** is a top view showing a position relationship between the end of the rib and the location at which the application of the fluorescent paste is finished according to an embodiment of the present invention.

FIG. **18** is a top view showing modified ribs on the substrate to which the present invention is applied.

FIG. **19** is a side view showing a modified tip of the nozzle according to the present invention.

FIG. **20** is a perspective view showing an application head which is another modified nozzle according to the present invention.

FIG. **21** is a longitudinal cross-sectional view of the application head shown in FIG. **20**.

FIG. **22** is a cross-sectional view along the line A—A of FIG. **21**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The plasma display panel (PDP) according to the present invention is constructed in such a manner that an electric

discharge is locally generated between a pair of opposing substrates so that the partitioned fluorescent layers on the substrate are excited to emit light. The PDP is constituted, for example, by a pair of substrate assemblies **50**, **50***a* shown in FIG. **1** (for one pixel).

In the substrate assembly **50***a*, a pair of sustaining electrodes X, Y are arranged per each line on the inside surface of a front-side glass substrate 11 for generating a surface discharge along the substrate surface. Each of the sustaining electrodes X, Y includes a wide linear band-like transparent electrode **41** made of a thin ITO film and a narrow linear band-like bus electrode **42** made of a thin metal film.

The bus electrode **42** is an auxiliary electrode for securing a proper electric conductivity. A dielectric layer **17** is provided so as to cover the sustaining electrodes X, Y. A protective film **18** is deposited by vaporization on the surface of the dielectric layer **17**. Both the dielectric layer **17** and the protective film **18** have a light transmission property.

In the substrate assembly **50**, address electrodes A are arranged on the inside surface of the rear-side glass substrate **21** so that the address electrodes A are perpendicular to the sustaining electrodes X, Y. A linear rib r is disposed in each interval formed between two adjacent address electrodes A. In other words, ribs r and address electrodes A are alternately disposed.

In the substrate assembly **50** (hereafter referred to as "substrate"), these ribs r serve to partition the electric discharge space **30** in the line direction per each subpixel (light emitting region unit) EU and define the gap dimension of the discharge space **30**.

Fluorescent layers **28** for displaying three colors R, G, and B are disposed so as to cover the rear-side walls including the upper portion of the address electrodes A and the side surface of the ribs r.

The ribs r are made of a low melting point glass and are opaque against ultraviolet rays. The ribs r may be formed through a process of providing an etching mask by photolithography on a solid-film low melting point glass layer to carry out patterning with a sandblast. The arrangement of the plurality of ribs to be formed in this process are determined by the pattern of the etching mask. Top views of the substrates showing preferable arrangements of the ribs are given in FIGS. **8**, **9**, and **18**. FIG. **8** shows a parallel arrangement in which the ribs are arranged in parallel with each other. FIG. **9** shows a meandering arrangement in which the ribs meander. FIG. **18** shows an arrangement in which a plurality of ribs r having a straight central portion and opposite ends bent in opposite directions are arranged on the substrate so that two adjacent ribs r leave each other at one end of the groove therebetween and approach each other at the other end of the groove and are parallel to each other at the central portion thereof.

Each pair of sustaining electrodes **12** corresponds to each line in a matrix display. Each address electrode A corresponds to each row. Three rows correspond to one pixel (picture element) EG. In other words, one pixel EG includes three subpixels EU arranged in the line direction, each subpixel representing one of the three colors R, G, and B.

An electric discharge generated between the address electrode A and the sustaining electrode Y controls the state of accumulated wall charge in the dielectric layer **17**. Application of sustaining pulses alternately onto sustaining electrodes X, Y induces generation of surface discharge (main discharge) in a subpixel EU where a certain amount of wall charge is present.

Being excited locally by the ultraviolet rays generated through the surface discharge, the fluorescent layers **28** emit visible light of respective colors. This visible light, transmitted through the glass substrate **11**, forms the displaying light. Since the arrangement pattern of the ribs **29** is what is known as a stripe pattern, the portion of the discharge space **30** corresponding to each row is continuous along the row and extends over all the lines. The emitted color of a subpixel EU in each row is the same.

In manufacturing such a PDP, the fluorescent layers are formed in a fluorescent layer forming apparatus after the address electrodes A and the ribs **29** are formed on the substrate, as shown in FIG. **1**. The platform for mounting the substrate in a fluorescent layer forming apparatus according to the present invention is not specifically limited and may be any platform onto which a substrate can be approximately horizontally and detachably fixed.

The paste-like fluorescent substance (fluorescent paste) for forming the fluorescent layers is, for example, a mixture of a fluorescent substance for each color at 10 to 50 wt%, ethyl cellulose at 5 wt%, and BCA at 45 to 85 wt%.

Here, the fluorescent substance for red may be, for example, (Y, Gd) $B0_3$: Eu. The fluorescent substance for green may be, for example, Zn_2SiO_4: Mn or $BaAl_{12}O_{19}$: Mn. The fluorescent substance for blue may be, for example, 3 (Ba, Mg) $O{\cdot}Al_2O_3$: Eu.

Referring to the nozzle of the dispenser for ejecting the fluorescent paste, the inner diameter of the nozzle is set so as to be smaller than the interval between adjacent ribs. However, since the tip of the nozzle is not inserted between the ribs, the outer diameter of the nozzle may be larger than the interval between adjacent ribs. For example, if the interval between the ribs is 170 μm, the nozzle may preferably have an inner diameter of about 100 μm and an outer diameter of about 300 μm. As the nozzle, a multi-nozzle may be used in which a plurality (for example, 5 to 30) of nozzles are arranged with a predetermined coating pitch along the direction perpendicular to the ribs. In such a case, a plurality of grooves are coated simultaneously, providing an efficient coating step.

The fluorescent paste supplier, namely, the dispenser for supplying fluorescent pastes into the grooves may include a nozzle, a vessel (syringe) connected to the rear end of the nozzle and containing the paste-like fluorescent substance, and a pressure generator for pressing the fluorescent substance in the vessel out into the nozzle. As the supplier, a commercially available dispenser system (for example, System C Type manufactured by Musashi Engineering Co., Ltd. in Japan) may be used.

The transporter to be used in accordance with the present invention may be one in which the nozzle and the platform are moved relative to each other so that the tip of the nozzle can be moved in three directions, namely, in the direction parallel to the ribs, in the direction perpendicular to the ribs on the substrate, and in the direction perpendicular to the substrate. Typical examples of the transporter are a three-axis robot and a three-axis manipulator.

A motor, an air cylinder, a hydraulic cylinder, or the like may be used as the driving force source for driving each of the axes according to the present invention. However, in view of the facility and accuracy of control, it is preferable to use a stepping motor or a servomotor equipped with an encoder.

The controller for controlling the moving operation of the transporter and the ejecting operation of the nozzle may consist of a microcomputer and a driver circuit. The microcomputer may include a CPU, a ROM, and an I/O port. The driver circuit drives the driving force source of the nozzle

transporter. A key board, a tablet, a mouse, or the like may be used as the input section for setting the controlling condition of the controller.

In the fluorescent layer forming apparatus constructed as shown above, a substrate with a plurality of parallel linear ribs formed on a surface thereof at a predetermined pitch is mounted on a platform. Subsequently, fluorescent layers are formed in each of the grooves between adjacent ribs by letting the fluorescent paste to eject from the tip of the nozzle while the tip of the nozzle is moved relative to the substrate.

If fluorescent pastes having different colors are to be applied into two adjacent grooves, there is a fear that the two fluorescent pastes are brought into contact and mix with each other by surface tension if a groove is coated with a fluorescent paste immediately after the adjacent groove is coated with another fluorescent paste. Therefore, it is preferable that, after a first groove is coated with a fluorescent paste of a first color and sufficiently dried, an adjacent second groove is coated with a fluorescent paste of a second color.

The conditions regarding the position and the dimension of the ribs such as the rib shape (linear or meandering shape), the rib length, the rib height, the pitch of arranged ribs, the number of arranged ribs, and the positions (coordinates) of the starting point and the end point of coating on the substrate, and the conditions regarding the nozzle such as the moving speed of the nozzle, the distance between the tip of the nozzle and the substrate (or the top of the rib), and the amount of ejected fluorescent paste per hour are set depending on the needs based on the input from the input section. This allows the controller to move the nozzle relative to the substrate in accordance with the rib position and the rib dimension that are thus set.

It is preferable that the fluorescent layer forming apparatus further includes an optical sensor for detecting alignment marks provided on the surface of the substrate. This is because detection of the alignment marks further facilitates recognition and correction of the nozzle position relative to the substrate position or rib position. An example of the optical sensor used in the present invention is a CCD camera.

If an optical sensor is used, alignment marks are formed in advance on the substrate surface corresponding to the position where the ribs are to be formed. In view of efficiency and accuracy, this step of forming the alignment marks is preferably performed simultaneously with the formation of the ribs.

In other words, if the ribs are formed by a printing method, the alignment marks are also simultaneously formed by the printing method. If the ribs are formed by a sandblast method, the alignment marks are also simultaneously formed by the sandblast method.

The controller detects the alignment marks that are thus formed and reads the coordinates thereof in advance by the optical sensor. In the coating process, the controller can thus judge the position and the pitch of each rib to move the nozzle or to modify the previously set position of the rib based on the alignment marks.

Here, the alignment mark may be provided either per each rib or per each prescribed number of ribs. The alignment marks provided at the starting position and at the finishing position of the coating makes it possible to accurately control the movement of the nozzle. The optical sensor may detect the front tip of the rib instead of the alignment mark. If the front tip of the rib is to be detected, it is preferable that dark ribs are formed by mixing a colorant such as a black

pigment into the rib material so as to provide a greater difference in brightness between the ribs and the grooves.

Referring to FIG. **12**, the amount Q ejected from the nozzle tends to increase as the distance C (hereafter referred to as "clearance") between the front tip of the nozzle and the substrate (or the top of the rib) increases. Accordingly, it is preferable to keep the clearance constant in the coating step.

Here, the clearance C is determined to be the most optimal value depending on the viscosity of the fluorescent paste and on the amount of the contained fluorescent substance. The clearance C is usually 100 to 200 μm. Conversely, by utilizing the above property, the amount Q ejected from the nozzle may be controlled by the clearance C.

Further, if the fluorescent paste is to be ejected between the ribs from the tip of the nozzle for coating, it has been confirmed that, once the coating is started, the fluorescent paste is pulled back to its normal position by its surface tension even when the tip of the nozzle is shifted a little bit from the normal coating position.

Utilizing this property, it is possible to carry out the coating operations smoothly by starting the coating with small clearance (that is, with a small amount of ejection) and restoring the clearance to the previously set distance after a predetermined time has passed so as to restore the ejected amount to the previously set value.

Accordingly, the coating step preferably includes a starting coating step for applying a fluorescent paste while maintaining the distance between the tip of the nozzle and the substrate to be a first distance, and a subsequent stationary coating step for applying the fluorescent paste while maintaining the distance between the tip of the nozzle and the substrate to be a second distance which is larger than the first distance.

Alternatively, an effective display region may be provided at a portion (a central portion) of the substrate surface and an ineffective display region may be provided at a portion (a periphery) of the substrate surface adjacent the effective region, whereby the starting coating step is carried out in the ineffective display region and the stationary coating step is carried out in the effective region.

Since the clearance C varies in accordance with the warping of the substrate or the variation in rib height, the clearance C must be corrected for each substrate. Correction of the clearance C can be performed by measuring the height of the substrate (or the rib) at (three or more) arbitrary points on the substrate to calculate a virtual curved surface (a spline curved surface) connecting the points, over which surface the tip of the nozzle is to be moved with a predetermined clearance C.

Accordingly, if the coating apparatus further comprises a height sensor for measuring the height of an arbitrary point on the substrate surface from the platform, the method for forming fluorescent layers preferably comprises a step of measuring the height of three arbitrary points on the substrate surface and a step of establishing a virtual curved surface connecting the measured points, whereby the tip of the nozzle is moved parallel to the virtual curved surface in the coating step.

Here, the height sensor may be a known optical sensor for determining the distance to an object by emitting a light from a laser diode to the object after high frequency modulation and comparing the phase of the reflected modulated wave with that of a standard wave.

FIGS. **2**, **3**, and **4** are a perspective view, a plan view, and a front view, respectively, of an apparatus for forming

fluorescent layers for a 42-inch color PDP. FIG. **5** is a block diagram of a controlling circuit of the apparatus.

Referring to these figures, pins **91** to **93** for positioning the substrate **50** are disposed to stand upright on the platform **51** for mounting the substrate **50**, and a sucking apparatus (not shown) is provided for fixing the substrate **50** onto the platform **51** by sucking.

A pair of Y-axis oriented transporters (hereafter referred to as "Y-axis robots") **52, 53** are disposed on both sides of the platform **51**. An X-axis oriented transporter (hereafter referred to as "X-axis robot") **54** is mounted onto the Y-axis robots **52, 53** so that the X-axis robot is movable in a direction shown by arrows Y–Y'. A Z-axis oriented transporter (hereafter referred to as "Z-axis robot") **55** is mounted onto the X-axis robot **54** so that the Z-axis robot is movable in a direction shown by arrows X–X'. On the Z-axis robot **55** is mounted a syringe attachment **58** for detachably attaching a dispenser including a nozzle **56** for ejecting a fluorescent paste and a syringe **57**, so that the syringe attachment **58** is movable in a direction shown by arrows Z–Z'. Position sensors **59, 60** for detecting the alignment marks on the surface of the substrate **50** are each independently mounted on the X-axis robot **54**, so that the sensors **59, 60** are movable in a direction shown by the arrows X–X'. Height sensors **61, 62** are provided for measuring the distance C (the clearance) from the tip of the nozzle **56** to the top of the rib and for measuring the distance from the tip of the nozzle **56** to the surface of the fluorescent paste after the fluorescent paste is applied. The height sensors **61, 62** are fixed onto the foot of the syringe attachment **58** so that the nozzle **56** is positioned between the height sensors **61, 62**.

The X-axis robot **54** is transported by Y-axis motors **52***a*, **53***a* in the Y-axis robots **52, 53**. The Z-axis robot **55** is transported by an X-axis motor **54***a* in the X-axis robot **54**. The position sensors **59, 60** are transported by sensor motors **54***b*, **54***c*, respectively. The syringe attachment **58** is transported by a Z-axis motor **55***a* in the Z-axis robot **55**.

Referring to FIG. **5**, the controller **80** includes a microcomputer having a CPU, a ROM, and a RAM and controls and drives the X-axis motor **54***a*, the Y-axis motors **52***a*, **53***a*, the Z-axis motor **55***a*, the sensor motors **54***b*, **54***c*, and an air controller **72** on receiving the output from the keyboard **81**, the position sensors **59, 60** and the height sensors **61, 62**. The controller **80** also lets the CRT **82** to display, in characters and images, the various conditions inputted from the keyboard **81** and the progress of the operation of applying the fluorescent paste.

Air pressure from an air source **70** (for example, an air bomb) is applied to the air controller **72** via an air tube **71**. On receiving the output from the controller **80**, the air controller **72** applies the air pressure to the syringe **57** via the air tube **73** to keep the amount ejected from the nozzle **56** to be constant.

The procedure for forming fluorescent layers on a substrate for a 42-inch PDP using the apparatus of the present invention will be hereinafter explained in conjunction with the flow chart shown in FIG. **6**.

First, the syringe **57** containing 20 cc of a fluorescent paste for forming red (R) fluorescent layers is attached together with the nozzle **56** to the syringe attachment **58**.

Referring to FIG. **7**, the substrate **50** having an ineffective display (dummy) region **50***b* around the effective display region **50***a* is mounted and fixed at a predetermined position on the platform **51** (step **S1**).

The substrate **50** consists of a glass plate having a thickness of about 3.0 mm. On the effective display region **50***a* of the substrate **50** are formed, in advance, 1921 ribs r having a length of L=560 mm, a height of H=100 μm, and a width of W=50 μm and being parallel to the direction shown by the arrows X–X' with a pitch P, as shown in FIG. **8**. On the dummy region **50***b* are formed, in advance, an alignment mark **M1** indicating the beginning position of the coating, an alignment mark **M2** indicating the center of the substrate, and an alignment mark **M3** indicating the end position of the coating, as shown in FIG. **7**. Since 1920 grooves are formed on the substrate **50** by 1921 ribs r, the fluorescent materials R, G, and B are each applied on 640 (1920/3) grooves, respectively.

At the time of fixing the substrate, the set values such as the rib height H, the rib width W, the number N of the ribs, the clearance C, the amount Q ejected from the nozzle, the thickness of the fluorescent paste to be applied, the velocity V of nozzle movement, and the coordinates of the height detection regions **R1** to **R9** (See FIG. **7**) are inputted from the keyboard **81**.

When the keyboard **81** is operated, the controller **80** detects the condition of the substrate and performs calculation operations (step **S2**). Specifically, by driving the X-axis robot **54** and the Y-axis robots **52, 53**, the controller **80** reads the position of the alignment mark **M2** via the position sensor **59**, and reads the positions of the alignment marks **M1, M3** via the position sensor **60**.

The controller **80** then detects, via the height sensor **61**, the points **P1** to **P9** having the maximum substrate height (the height from the platform **51**) in the set regions **R1** to **R9**, respectively. Further, the controller **80** calculates coordinates of the starting point for coating, the coating pitch P, the spline curved surface passing through the points P1 to P9, and the like. Here, the pitch P is calculated from the distance between the marks M1 and M2 and the number N of the ribs.

Then, the operator attaches to the syringe attachment **58** a syringe (with a nozzle) containing a red fluorescent paste (hereafter referred to as "R fluorescent paste") as a syringe **57** and a nozzle **56** (step **S4**). When the starting operations are performed on the keyboard **81** (step **S5**), the tip of the nozzle **56** is moved, based on the alignment mark **M1**, to the starting point for coating the R fluorescent paste and is maintained at a predetermined height (the clearance) (step **S6**).

The nozzle **56** then begins to eject the R fluorescent paste and, at the same time, moves in the direction shown by the arrow X, thereby starting the operation of applying the fluorescent paste (step **S7**). When the nozzle **56** moves by the length L of one rib, the nozzle **56** stops performing the ejecting and moving operations (operation of applying the fluorescent paste) (step **S8** and step **S9**).

The nozzle **56** then moves for a pitch 3P in the direction shown by the arrow Y and begins the ejecting operation and the moving operation in the direction shown by the arrow X' (steps **S10** to **S12**). After moving by length L, the nozzle **56** stops the ejecting and moving operations and moves for a pitch 3P in the direction shown by the arrow Y (steps **S13** to **S16**). The nozzle **56** repeats the operations in the steps S7 to S16 and, when the number of coated grooves reaches **640** in the step **S10** or **S15**, the work with the R fluorescent paste is completed.

The operator then replaces the syringe **57** and the nozzle **56** with those for green fluorescent paste (hereafter referred to as "G fluorescent paste") and repeats the operations in the steps **S5** to **S16** (steps **S17, S18**). After the coating of **640** grooves with the G fluorescent paste is finished, the syringe **57** and the nozzle **56** are replaced with those for a blue

fluorescent paste (hereafter referred to as B fluorescent paste), and the coating of **640** grooves with the B fluorescent paste is conducted in the same manner as mentioned above (steps S**19**, S**20**).

Here, the above coating operation is stopped so that a portion coated with the fluorescent paste **28** in each of the grooves is shorter than the groove by a predetermined distance , as shown in FIG. **17**. This is for preventing the applied fluorescent paste from being extended around the end of the rib r into an adjacent groove. In this case, it has been experimentally shown that a distance d of more than 0.5 mm is sufficient.

The coating operation of the above embodiment is constructed in such a manner that, on finishing the application of the fluorescent paste into one groove, the nozzle **56** is moved in the direction shown by arrow Y by a predetermined pitch 3p so as to start the application of the fluorescent paste into the next groove. Alternatively, however, the coating operation may be performed by detecting, with the position sensors **59**, **60**, the front end and the rear end, respectively, of the rib forming the next groove to be coated every time the coating operation of one groove is finished, and by moving the nozzle **56** on the basis of the detected front and rear ends of the rib. This further improves the precision of applying the fluorescent paste into each groove. In this case, if the position sensors **59** and **60** cannot detect the front end or the rear end of the rib due to a certain cause (for example, a partial destruction of the rib end), the coating operation of applying the fluorescent paste into the next groove is performed on the basis of the predetermined rib pitch without discontinuing the coating operation.

When all the operations for forming R, G, and B fluorescent layers fitted onto the interior surface of the grooves between the ribs as shown in FIG. **1** are finished, the X-axis robot **54** returns to the home position (the position nearest to the upper perimeter of the platform **51** in the direction shown by the arrow Y' in FIG. **3**). The operator then discharges the substrate **50** (step S**21**). The fluorescent paste on the discharged substrate **50** is dried in the subsequent step.

Here, in the above operation of applying the fluorescent paste, the tip of the nozzle **56** is maintained by the Z-axis robot **55** at a height such that the tip of the nozzle **56** is always away by the clearance C=100 μm from the calculated spline curved surface.

While the coating operation is performed in the directions shown by arrows X and X', the controller **80** watches the surface height (the thickness) of the fluorescent paste immediately after the application with the height sensor **62** and the height sensor **61**, respectively. When the thickness of the applied fluorescent paste measured by the height sensors **62** and **61** deviates from a predetermined permissible range, the controller **80** immediately stops the coating operation (ejection and movement) of the nozzle **56**. The controller **80** then lets an alarm indicating "poor application" and coordinates of the position of the stopped nozzle **56** to be displayed on the CRT **82**. The controller **80** also stores the coordinates into the built-in RAM.

After the cause of the poor application (for example, the clogging of the nozzle) is removed, the operator replaces the substrate **50** on the platform **51** with a new one to start the coating operation again (steps S**1** to S**21**).

This enables the "poor application" of the fluorescent paste to be detected much earlier than by the conventional method of inspecting the substrate after the three colors of R, G, and B have been applied and the drying step has been finished. Therefore, the efficiency and the yield in applying the fluorescent paste is improved. Also, since the RAM stores the position (coordinates) at which the "poor application" has occurred on the substrate, it is easy to perform the repairing or reapplying operation on the substrate.

In this Example, the substrate **50** was used having a plurality of ribs r independently formed on the surface as shown in FIG. **8**, Alternatively, however, a substrate may be used in which the ends of the adjacent ribs are alternately connected with each other as shown in FIG. **9**. According to such a rib shape, the connecting portion of the ends becomes an end position of coating for each fluorescent paste, so that the webbing (stringing) of the fluorescent paste at this portion can be prevented.

Further, it is preferable that the substrate to be used has such ribs r that two adjacent ribs leave each other at one end of the groove between the ribs and approach each other at the other end of the groove, as shown in FIG. **18**, and the coating operation is started at the wider end of the groove and is finished at the narrower end of the groove. This is to ensure that the fluorescent paste **28** is easily introduced into the groove at the time of starting the coating operation and is prevented from being forced out of the groove at the time of finishing the coating operation.

In this Example, the alignment marks **M1** and **M3** are detected for calculating the pitch P of the ribs r. Alternatively, however, auxiliary alignment marks m may be provided for every predetermined number of ribs, as shown in FIG. **10**, and a pitch P of the ribs may be set in advance before the coating operations so that the pitch P may be corrected by the detection of the marks m with the position sensor **59** or **60** during the coating operations. The alignment marks **M1**, **M2**, **M3**, and m are formed simultaneously when the ribs r are formed on the substrate **50**.

Alternatively, the pitch P may be set in advance before the coating operations and the position of the last rib to be coated may be calculated from the pitch P. The nozzle **56** is moved to the coordinate point corresponding to the rib as shown in FIG. **11** to draw a point T with the fluorescent paste. The coordinates of the point T and the coordinates of the alignment mark **M3** are detected by the position sensor **60**. The set pitch P is corrected by their distance difference ΔL.

FIG. **13** is a view for explaining a construction of a system utilizing the apparatus shown in FIG. **2**, in which an apparatus **100**R for forming R fluorescent layers, a drying furnace **200***a*, an apparatus **100**G for forming G fluorescent layers, a drying furnace **200***b*, an apparatus **100**B for forming B fluorescent layers, and a drying furnace **200***c* are connected in series via conveyors **300***a* to **300***e*. All of the apparatus **100**R for forming R fluorescent layers, the apparatus **100**G for forming G fluorescent layers, and the apparatus for forming B fluorescent layers are similar to the fluorescent layer forming apparatus shown in FIG. **2**. In this example, however, each of the syringes **57** contains one of an R fluorescent paste, a G fluorescent paste, and a B fluorescent paste.

In this construction, after **640** R fluorescent layers are formed on the surface of the substrate **50** (FIG. **7**) by the R fluorescent layer forming apparatus **100**R, the substrate **50** is transported to the drying furnace **200***a* by the conveyor **300***a* to be dried. The dried substrate **50** is transported to the G fluorescent layer forming apparatus **100**G by the conveyor **300***b* for forming **640** G fluorescent layers on the surface of the substrate **50**.

The substrate **50** is then transported to the drying furnace **200***b* by the conveyor **3006***c* to be dried. The dried substrate

50 is transported to the B fluorescent layer forming apparatus 100B by the conveyor 300*d* for forming 640 B fluorescent layers on the surface of the substrate 50.

The substrate 50 is further transported to the drying furnace 200*c* by the conveyor 300*e* to be dried. Subsequently, the substrate 50 is sintered with a sintering apparatus (not shown) to complete the R, G, and B fluorescent layers 28 fitted onto the interior surface of the grooves between the ribs 29 as shown in FIG. 1.

In the drying furnaces 200*a* to 200*c*, the fluorescent paste which fills the grooves on the substrate 50 is dried at a temperature of 100 to 200° C. for 10 to 30 minutes to form the fluorescent layer as mentioned above. The drying processes are conducted immediately after the fluorescent paste for each color is applied into the grooves because of the following reason. If the adjacent fluorescent paste previously applied is in a liquid state, the fluorescent paste subsequently applied extends over the rib to be mixed with the previous fluorescent paste by their surface tensions when being in contact, causing a mixed color. By subjecting the substrate to a drying step, the fluorescent paste filling the grooves between the ribs is fitted onto the interior surface of the grooves, thereby losing its surface tension. For the drying furnaces 200*a* to 200*c*, at least one of a hot plate method, a circulated hot air method, and a far infrared light method is employed.

FIG. 14 is a view for explaining a construction of another system utilizing an apparatus as shown in FIG. 2. In this embodiment, one drying furnace 200 is provided instead of the three drying furnaces 200*a* to 200*c* as shown in FIG. 13. Instead of the conveyors 300*a* to 300*e*, a transporting robot 300 is provided for transporting the substrate 50 in a direction shown by arrows A–A' and in a direction shown by arrows B–B'.

In this construction, the substrate 50 is transported to the drying furnace 200 by the transporting robot 300 to be dried every time a fluorescent paste of each color is applied to the grooves in the same manner as in the system shown by FIG. 13.

FIG. 15 and FIG. 16 are a perspective view and a cross-sectional view showing a multi-nozzle as a modification of the syringe 57 and the nozzle 56 to be used in each of the above-described Examples.

In this multi-nozzle, six nozzles 56*a* are arranged in a line per each syringe 57*a* with a pitch six times longer than the rib pitch P.

When a fluorescent paste is applied, the fluorescent paste contained in the syringe 57*a* is ejected through the six nozzles 56*a* simultaneously. Therefore, six fluorescent layers of a color are formed at a time, thereby curtailing the time required for the coating operations to one sixth (1/6) as compared with each of the previously described Examples.

Now, the relationship between the rib pitch P, the nozzle pitch P_N, and the amount of movement of the nozzle in the Y direction will be explained when a multi-nozzle is used having n nozzles arranged in a line at a pitch of P_N per each syringe (Here, it is assumed that the fluorescent pastes are provided in three colors of R, G, and B).

[A] The case where the fluorescent paste is applied while the nozzle is being moved in forward and backward directions.

The substrate shown in FIG. 8, FIG. 9, or FIG. 18 (especially the substrate having ribs in which the ends of the adjacent ribs are alternately open as shown in FIG. 9 or FIG. 18) may be used. The pitch P_N of nozzle arrangement is set so that P_N is 6P and the coating operation is carried out as follows.

(1) Applying the fluorescent paste simultaneously into n grooves at an application pitch of 6P while moving the nozzle in the X direction from the open guide (the opening of the first groove) of the end pattern of the rib, (2) Moving the nozzle in the Y direction by a distance of 3P so as to locate the nozzle at an open side of the end pattern of the rib (the opening of the second groove), (3) Applying the fluorescent paste newly into n grooves while moving the nozzle in the X' direction (Through the above steps, the fluorescent paste has been applied into 2n grooves at a pitch of 3P), (4) Moving the nozzle in the Y direction by a distance of 3P×(2n−1) so as to locate the nozzle at the opening of the third groove.

The above steps (1) to (4) are repeated.

[B] The case where the fluorescent paste is applied while the nozzle is being moved in one direction

The substrate shown in FIG. 8 may be used. The pitch P_N of nozzle arrangement is set so that P_N is 3P and the coating operation is carried out as follows.

(1) Applying the fluorescent paste simultaneously into n grooves at an application pitch of 3P while moving the nozzle in a forward direction (in the X direction or in the X' direction),

(2) Moving the nozzle in a backward direction without applying the fluorescent paste so as to return the nozzle to the point of starting the application of the fluorescent paste,

(3) Moving the nozzle in the Y direction by a distance of 3P×n.

The above steps (1) to (3) are repeated.

In this manner, when the coating operation is carried out simultaneously with a plurality of nozzles 56*a*, it is difficult to apply the fluorescent paste uniformly and accurately into the groove corresponding to each nozzle if the end surface of the tip of the nozzle is perpendicular to the axis of the nozzle, even though the pitch of the nozzle is let to coincide with the rib pitch with high precision. This is because the fluorescent paste cannot be easily ejected immediately under the tip of the nozzle due to the viscosity and the surface tension of the fluorescent paste.

Therefore, when a plurality of nozzles are to be used, it is preferable that each of the nozzles has an end surface formed at an acute angle of θ relative to the axis of the nozzle, as shown in FIG. 19. Also, it is preferable that the nozzle is held at an acute angle of θ relative to the substrate 50 in the direction of applying the fluorescent paste so that the opening of the tip of the nozzle is oriented in a direction opposite to the direction of applying the fluorescent paste. In such a case, the angle θ is set to be within the range of 30° to 60°, and the angle CL is set to be within the range of 45° to 70°. This makes it possible to eject the fluorescent paste from each of the nozzles with certainty in the direction opposite to the direction of applying the fluorescent paste, thereby fixing the direction of ejection. Thus, each of the nozzles can apply the fluorescent paste with accuracy into each of the intended grooves.

The syringe 57*a* is attached to the syringe attachment 58 (FIG. 4) so that each of the nozzles 56*a* is arranged perpendicular to the ribs. However, when a mechanism is provided for rotating the syringe 57*a* in a direction shown by an arrow W in FIG. 15, the rotation of the syringe 57*a* makes it possible to adjust the coating pitch of the nozzles 56*a*.

Further, according to the present invention, it is possible to conduct fluorescent paste application similar to the one for the above-described multi-nozzle by using a head 63 shown in FIG. 20 obtained by improving the applicator head of a coating apparatus called a slot-die coater or a die-coater for applying a curtain-like paste.

The longitudinal cross section of the head **63** is shown in FIG. **21**, and the cross section of FIG. **21** along the A—A line is shown in FIG. **22**. As shown in these Figures, the head **63** includes therein a reservoir tank **57*b*** for temporarily storing the fluorescent paste and a plurality of gaps (channels) **56*b*** for ejecting the fluorescent paste, the gap corresponding to the nozzle **56*a*** in FIG. **16**. Through these channels **56*b***, the fluorescent paste is ejected in a manner like the teeth of a comb. For forming the above-described fluorescent layers of the three colors, the heads **63** corresponding to each of the three colors are arranged as mentioned above for completing the entire coating operations.

According to the present invention, a fluorescent paste can be ejected from a nozzle moving over a substrate so as to be applied into the grooves between the ribs without the use of a conventional screen mask and by simply setting the substrate design numerically. Therefore, it is possible to form fluorescent layers accurately on a substrate of any size and to easily comply with a change in substrate design.

What we claim is:

1. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser for ejecting the fluorescent paste, comprising a plurality of nozzles spaced corresponding to a predetermined number of grooves for ejecting the fluorescent paste, whereby the fluorescent paste is applied simultaneously into a plurality of grooves;

a transporter for moving the nozzles relative to the platform; and

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into the selected grooves.

2. An apparatus for forming fluorescent layers according to claim **1**, wherein the controller further performs a function of controlling the transporter and the dispenser on the basis of a predetermined rib pitch.

3. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste;

a transporter for moving the nozzle relative to the platform; and

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into selected grooves, and so that a step of applying the fluorescent paste is started while maintaining a distance between the nozzle and the substrate to be a first distance and the step of applying the fluorescent paste is subsequently continued while maintaining the distance between the nozzle and the substrate to be a second distance larger than the first distance.

4. An apparatus for forming fluorescent layers according to claim **3**, wherein the substrate to be used comprises an effective display region at a central portion thereof and an ineffective display region around the effective display region, and the controller controls the transporter and the dispenser so that the fluorescent paste is applied while maintaining the distance between the nozzle and the substrate to be the first distance over the ineffective display region and to be the second distance over the effective display region.

5. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate having an alignment mark formed on the surface thereof, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste;

a transporter for moving the nozzle relative to the platform;

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into selected grooves; and

a position sensor for detecting a position of at least one of the alignment mark and a rib tip on the substrate, whereby the controller further performs a function of controlling the transporter and the dispenser on the basis of the position detected by the position sensor.

6. An apparatus for forming fluorescent layers according to claim **5**, wherein the controller further performs a function of predetermining a pitch of applying a fluorescent paste and a function of correcting the predetermined pitch on the basis of at least one of the alignment mark and the rib end detected by the position sensor.

7. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste;

a transporter for moving the nozzle relative to the platform;

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into selected grooves; and

a height sensor for measuring a height of an arbitrary point on the substrate from the platform, the controller adjusting the distance between the nozzle and the substrate at the time of applying the fluorescent paste on the basis of the height measured by the height sensor.

8. An apparatus for forming fluorescent layers according to claim **7**, wherein the controller further performs functions of measuring the height of arbitrary three points on the surface of the mounted substrate or on the ribs in advance with the height sensor, of establishing a virtual curved surface connecting the measured points, and of controlling the transporter and the dispenser so that the tip of the nozzle is moved parallel to the virtual curved surface to apply the fluorescent paste into the grooves.

9. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste;

a transporter for moving the nozzle relative to the platform;

a thickness sensor for measuring the thickness of the fluorescent paste applied into the groove; and

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively

applied into selected grooves, and for stopping the application of the fluorescent paste when the thickness measured by the thickness sensor deviates from a predetermined permissible range.

10. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel at a predetermined rib pitch on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste;

a transporter for moving the nozzle relative to the platform;

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into selected grooves; and

a position sensor for detecting an end of the rib, wherein the controller further performs a function of controlling the transporter and the dispenser on the basis of the detected end when the end is clearly detected by the position sensor and on the basis of the predetermined rib pitch when the end cannot be clearly detected.

11. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste;

a transporter for moving the nozzle relative to the platform; and

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into and coated on selected grooves and so that the length of a coated portion of the groove is shorter than the length of the entire groove by a predetermined distance.

12. An apparatus for forming fluorescent layers in a plasma display panel by applying a fluorescent paste into grooves formed between a plurality of ribs disposed in parallel on a surface of a substrate, the apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having at least one nozzle for ejecting the fluorescent paste, the nozzle having an end surface formed obliquely relative to the axis of the nozzle;

a transporter for moving the nozzle relative to the platform; and

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into selected grooves.

13. An apparatus for forming fluorescent layers according to claim **12**, wherein the nozzle is held at an acute angle with the substrate in the direction of applying the fluorescent paste.

14. A method for manufacturing one of a pair of substrate assemblies constituting a color plasma display panel, the manufactured substrate assembly having fluorescent layers of three different colors, the method comprising:

a rib formation step of forming a plurality of ribs having a straight central portion and opposite ends bent in such a manner that the opposite ends are bent in opposite directions, and arranging the ribs on a substrate for the substrate assembly so that two adjacent ribs leave each other at one end of the groove therebetween and approach each other at the other end of the groove and are parallel to each other at the central portion thereof as seen from above the substrate; and

a coating step of applying a fluorescent paste of one color into a groove formed between two adjacent ribs by moving a nozzle for ejecting the fluorescent paste along the groove, the movement of the nozzle being started from an end of the groove where the two adjacent ribs leave each other, wherein the fluorescent paste of the one color is applied into every third groove formed between ribs by consecutive reciprocating movement of the nozzle along the grooves in the coating step.

15. A system, comprising:

a plurality of apparatuses for respectively forming fluorescent layers having different respective colors in grooves on a substrate, each apparatus comprising:

a platform for mounting the substrate thereon;

a dispenser having a nozzle to eject fluorescent paste;

a transporter for moving the nozzle relative to the platform; and

a controller for controlling the transporter and the dispenser so that the fluorescent paste is consecutively applied into selected grooves.

16. A system according to claim **15**, wherein the apparatuses are arranged in a series, the system further comprising:

a plurality of dryers each provided between the fluorescent layer forming apparatus, each of the dryers serving to dry the fluorescent paste applied into the grooves between the ribs on the substrate; and

a plurality of substrate transporters provided for transporting the substrate between each of fluorescent layer forming apparatus and each of the dryers.

17. A system for forming fluorescent layers according to claim **16**, wherein:

each of the fluorescent layer forming apparatus consecutively applies each fluorescent paste into the grooves on the substrate, the grooves corresponding to the color of the fluorescent paste;

each of the dryers dries the fluorescent paste in the grooves between the ribs on the substrate to such a degree that at least no surface tension is generated; and

each of the substrate transporters transports the substrate having the fluorescent paste thereon from one of the fluorescent layer forming apparatus to the next fluorescent layer forming apparatus adjacent thereto via one of the dryers,

so that the filling and the drying of the fluorescent paste of each color are alternately conducted, the drying process serving to allow the fluorescent layers to be deposited onto interior surfaces of the grooves between the ribs.

18. A system according to claim **15**, further comprising:

a dryer for drying the substrate; and

a substrate transporter for transporting the substrate between each of the fluorescent layer forming apparatus and the dryer.

19. A system for forming fluorescent layers according to claim **18**, wherein:

each of the fluorescent layer forming apparatus consecutively applies a fluorescent paste into grooves on the substrate, the grooves corresponding to the color of the fluorescent paste;

the dryer dries the fluorescent paste in the grooves between the ribs on the substrate to such a degree that at least no surface tension is generated; and

the substrate transporter transports the substrate having the fluorescent paste thereon from one of the fluorescent layer forming apparatus to another of the fluorescent layer forming apparatus via the dryer,

so that the filling and the drying of the fluorescent paste of each color are alternately conducted, the drying process serving to allow the fluorescent layers to be deposited onto interior surfaces of the grooves between the ribs.

20. A method for consecutively applying a plurality of fluorescent pastes having different colors into grooves formed between a plurality of ribs disposed in parallel on a substrate surface, the different colors including at least first and second colors, the method comprising the steps of:

preparing a plurality of fluorescent layer forming apparatus each ejecting a fluorescent paste of each color;

applying the fluorescent paste of the first color into first grooves on the substrate surface with one of the fluorescent layer forming apparatus, the first grooves corresponding to the fluorescent paste of the first color;

drying the fluorescent paste of the first color applied into the first grooves to such a degree that at least no surface tension is generated;

applying the fluorescent paste of the second color subsequently with another of the fluorescent layer forming apparatus into second grooves adjacent the first grooves on the substrate, the second grooves corresponding to the fluorescent paste of the second color; and

drying the fluorescent paste of the second color applied into the second grooves to such a degree that at least no surface tension is generated, and alternately repeating the steps of applying and drying the fluorescent paste of each color.

21. A method for applying fluorescent pastes according to claim **20**, wherein each fluorescent layer forming apparatus comprises a dispenser having a plurality of nozzles, the nozzles being spaced at a rib pitch which is an integer multiple of the number of the colors, whereby the fluorescent paste of each color is simultaneously ejected to fill a plurality of different grooves on the substrate.

22. A method for applying fluorescent pastes according to claim **20**, wherein the fluorescent paste in the grooves between the adjacent ribs is fitly deposited onto interior surfaces of the grooves to lose its surface tension in the drying step.

23. A method for applying fluorescent pastes according to claim **20**, wherein each fluorescent layer forming apparatus comprises a dispenser for ejecting a fluorescent paste.

24. A method for applying fluorescent pastes of three different colors into grooves between a plurality of ribs spaced in parallel at a pitch P on a substrate, wherein a fluorescent paste dispenser comprises n nozzles spaced at a pitch of 6P, the method comprising repetition of the steps of:

(1) applying a fluorescent paste simultaneously at the pitch of 6P into n grooves with the n nozzles while moving the dispenser in a forward direction;

(2) moving the dispenser by a distance of 3P in a direction perpendicular to the ribs;

(3) applying the fluorescent paste into n grooves while moving the dispenser in a backward direction; and

(4) moving the dispenser by a distance of $3P\times(2n-1)$ in the direction perpendicular to the ribs.

25. A method for applying fluorescent pastes according to claim **24**, wherein the substrate to be used has such ribs that ends of an adjacent pair of ribs are alternately connected so that the ribs meander.

26. A method for applying fluorescent pastes according to claim **24**, wherein the substrate to be used has such ribs that two adjacent ribs leave each other at one end of the groove therebetween and approach each other at the other end of the groove.

* * * * *

US006416174B1

(12) **United States Patent**
Ito et al.

(10) **Patent No.: US 6,416,174 B1**
(45) **Date of Patent: Jul. 9, 2002**

(54) **INK COMPOSITION, PATTERN FORMING METHOD, AND COLOR FILTER**

(75) Inventors: **Takeo Ito**, Kumagaya; **Kazuo Sakai**, Kawanishi; **Hiroyuki Nakazumi**, Kawachinagano, all of (JP)

(73) Assignees: **Kabushiki Kaisha Toshiba**, Kawasaki; **Fuji Pigment Co., Ltd.**, Kawanishi, both of (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/250,483**

(22) Filed: **Feb. 16, 1999**

Related U.S. Application Data

(62) Division of application No. 08/781,727, filed on Jan. 10, 1997.

(30) **Foreign Application Priority Data**

Jan. 11, 1996 (JP) 8-003372

(51) **Int. Cl.**[7] **G01D 11/00**
(52) **U.S. Cl.** **347/100**; 347/96
(58) **Field of Search** 347/100, 96, 101

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,965,278 A		6/1976	Duinker et al.	313/466
4,957,553 A	*	9/1990	Koike et al.	106/31.58
5,079,214 A	*	1/1992	Long et al.	428/195
5,180,425 A		1/1993	Matrick et al.	106/22 R
5,302,197 A		4/1994	Wickramanayke et al.	106/22 H
5,376,169 A		12/1994	Horomi et al.	523/160
5,401,303 A		3/1995	Stoffel et al.	106/31.86
5,693,127 A	*	12/1997	Nigam et al.	347/100
5,700,609 A	*	12/1997	Matsuda et al.	430/27

FOREIGN PATENT DOCUMENTS

EP	622 429		11/1994	
EP	688 835		12/1995	
EP	0735120 A2	*	10/1996	C09D/11/00
JP	59-75205		4/1984	
JP	05224007 A	*	9/1993	G02B/5/20
JP	05224008 A	*	9/1993	G02B/5/20
JP	7-17911		7/1995	

OTHER PUBLICATIONS

Translation of Selected Portions of JP 7–179711.

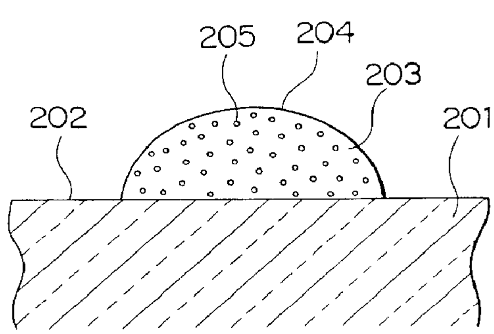
* cited by examiner

Primary Examiner—John Barlow
Assistant Examiner—M Shah
(74) *Attorney, Agent, or Firm*—Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P.

(57) **ABSTRACT**

An ink composition having a pigment in its droplets, which are adhered onto the surface such as glass, ceramics or polyester resins of a base material, always dispersed uniformly is ejected from a nozzle by an ink-jet method to directly form a prescribed pattern of a colored layer of a color filter on the surface of the base material.

18 Claims, 2 Drawing Sheets



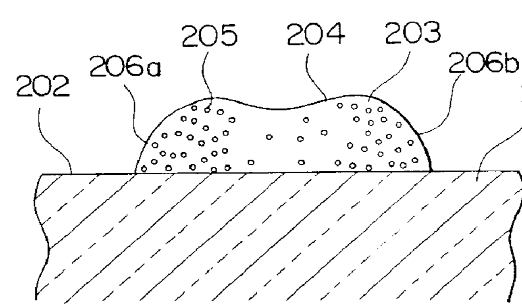


FIG. 1A

FIG. 1B

FIG. 1C

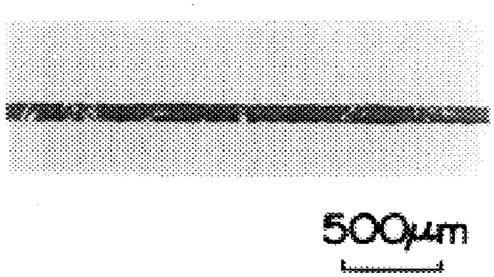


FIG. 1D

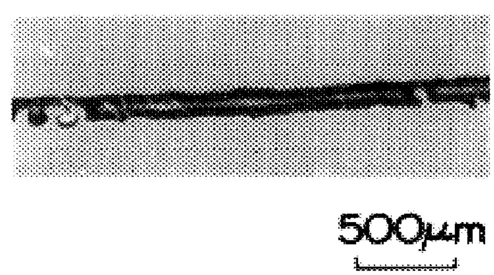


FIG. 2A

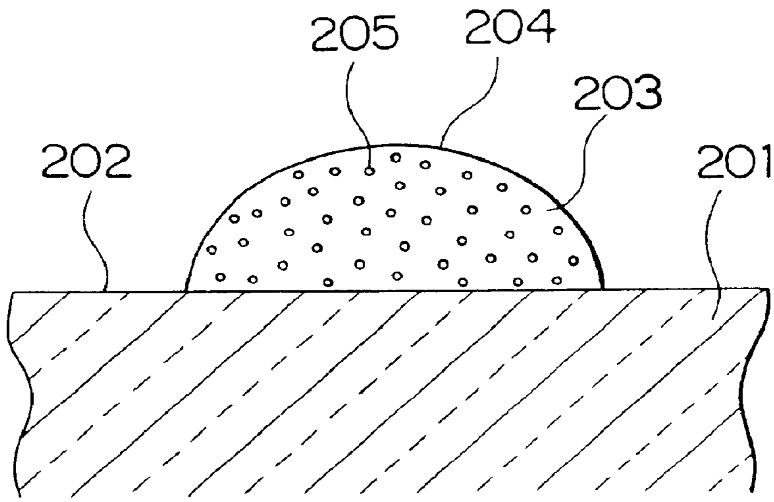
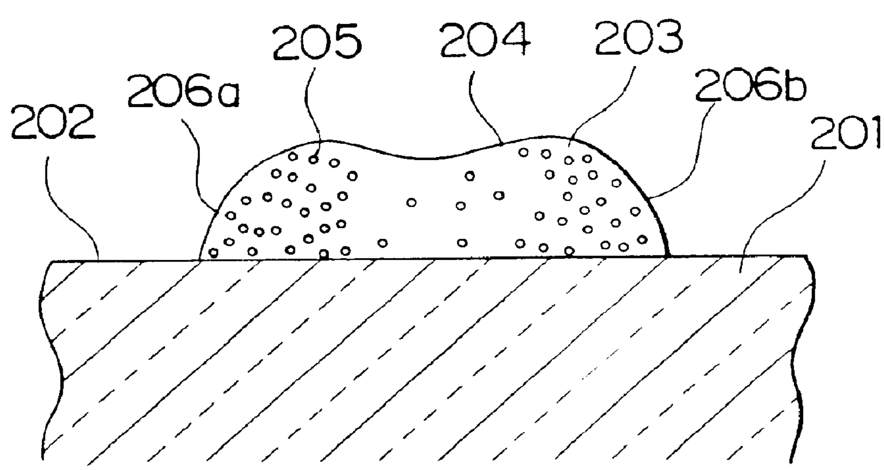


FIG. 2B



INK COMPOSITION, PATTERN FORMING METHOD, AND COLOR FILTER

This is a division of application Ser. No. 08/781,727, filed Jan. 10, 1997, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an ink composition, a pattern forming method and a color filter, and particularly to an ink composition used to form a pattern by an ink-jet method, a pattern forming method which uses the above ink composition, and a color filter which is produced by the pattern forming method using the above ink composition.

2. Description of the Related Art

The pattern forming method according to the ink-jet method sprays droplets of an ink composition onto a base material by various types of ink composition ejecting methods such as an electrostatic attraction method, a method which employs a piezoelectric element to mechanically vibrate or bias ink, or a method of heating to foam ink and using a pressure by the foamed ink to form a pattern on the surface of the base material. And, the pattern forming method according to the ink-jet method has advantages that a pattern can be formed quickly without involving production of large noise, and a multi-colored pattern can be formed easily. Therefore, it is attracting attention in many fields.

Meanwhile, color filters h are used for display units such as a CRT, a liquid crystal display and a plasma display, or a solid state image pickup device and the like have been produced by various types of methods such as a pigment dispersion method, a dye dispersion method, and a dyeing method.

For example, Japanese Patent Laid-Open Publication No. Hei 7-179711 describes a method of producing a fluorescent film with a filter by forming a patterned photo absorption layer on the inner face of a face plate, applying a pigment dispersed solution and a phosphor slurry, and exposing through a mask and developing. And, Japanese Patent Laid-Open Publication No. Sho 59-75205 describes a method of producing a color filter by forming a colored layer on a substrate by the ink-jet method.

However, the method of producing a fluorescent film with a filter described in Japanese Patent Laid-Open Publication No. Hei 7-179711 has a disadvantage that the production cost is high because it involves many steps to produce the fluorescent film, and the application of a pigment dispersed solution and a phosphor slurry and the exposure through a mask and development are required for each color. And, the method of producing a color filter described in Japanese Patent Laid-Open Publication No. Sho 59-75205 which forms a colored layer on a substrate by the ink-jet method has disadvantages that a dispersion preventive pattern or a wettability improver must be formed on a glass substrate in advance, increasing facilities investment and the number of processes, also increasing the production cost, and lowering a production yield.

The present invention has been completed in view of the above circumstances, and aims to provide an ink composition which can form a fine pattern on the surface of glass, ceramics or polyester resins by the ink-jet method without requiring to form a wettability improver.

The present invention also aims to provide a pattern forming method which can easily form a fine pattern efficiently on the surface of a glass substrate or the like, and does not involve many processes or facilities investment, so that the formed pattern excels in reliability and economy.

Besides, the present invention aims to provide a color filter having a pattern which excels in optical resistance and water resistance and has high reliability in practical use, and which also excels in economy.

SUMMARY OF THE INVENTION

An ink composition according to the present invention is controlled to keep maximum the ratio (V/S) of the volume (V) of a system which consists of a solvent, a pigment dispersed into the solvent and a dispersant which is dispersed into the solvent to enhance an affinity between the solvent and the pigment; and the surface area (S) of an interface of the system produced on a boundary between the system and a gas phase.

And, an ink composition according to the present invention has a system which consists of a solvent, a pigment dispersed into the solvent and a dispersant which is dispersed into the solvent to enhance an affinity between the solvent and the pigment, and the system has (1) a surface tension of 20.0 dyn/cm to 50.0 dyn/cm at 25° C., and (2) a viscosity of 1.5 cp to 20.0 cp at 25° C.

Besides, an ink composition according to the present invention contains a solvent, a pigment dispersed into the solvent, a dispersant which is dispersed into the solvent to enhance an affinity between the solvent and the pigment, and an additive which is dispersed into the solvent to control free energy of an interface.

A pattern forming method according to the invention has a step of ejecting from a nozzle by an ink-jet method droplets of an ink composition of which the ratio (V/S) between the volume (V) of a system which consists of a solvent, a pigment dispersed into the solvent and a dispersant which is dispersed into the solvent to enhance the affinity between the solvent and the pigment; and the surface area (S) of the interface of the system produced on at the boundary between the system and a gas phase is controlled to be kept at a maximum, a step of adhering the droplets onto the surface of a base material, and a step of adhering the pigment contained in the droplets onto the base material.

And, a pattern forming method according to the invention has a step of ejecting from a nozzle by an ink-jet method droplets of an ink composition having a system which consists of a solvent, a pigment dispersed into the solvent and a dispersant which is dispersed into the solvent to enhance an affinity between the solvent and the pigment, and which has (1) a surface tension of 20.0 dyn/cm to 50.0 dyn/cm at 25° C. and (2) a viscosity of 1.5 cp to 20.0 cp at 25° C., a step of adhering the droplets onto the surface of a base material, and a step of adhering the pigment contained in the droplets onto the base material.

Furthermore, a pattern forming method according to the invention has a step of ejecting from a nozzle by an ink-jet method droplets of an ink composition containing a solvent, a pigment dispersed into the solvent, a dispersant which is dispersed into the solvent to enhance an affinity between the solvent and the pigment, and an additive which is dispersed into the solvent to control free energy of an interface, a step of adhering the droplets onto the surface of a base material, and a step of adhering the pigment contained in the droplets onto the base material.

A color filter according to the invention has a base material and a colored layer which is formed of a pigment adhered to the surface of the base material by an ink-jet method.

Generally, to form a pattern of picture elements for a color filter by an ink-jet method, when a base material has a surface (to-be-colored layer) of glass, ceramics or a film material made of polyester resin or the like which is different from fiber of paper or the like, a conventional ink composition is not adequately adhered to the surface of such a base material, and the ink composition is repelled or spreads on the surface of the base material. And, since the adhesion of a coloring matter to the surface of the base material is weak, it is easily separated from the surface of the base material, and the formed pattern is broken in a short period. The base material used herein generally means those having a to-be-colored layer surface, onto which the coloring matter of the ink composition is adhered, with a structure of glass, ceramics or a film made of polyester resin or the like which is different from fiber of paper or the like. Therefore, the base materials belonging to such a category can be a glass substrate or a ceramics substrate; various types of film materials such as polyester resin, diacetate resin, triacetate resin, acrylic resin, polycarbonate resin, polyvinyl chloride resin, polyimide resin, cellophane or celluloid; and coated paper of which the surface is coated with organic polymer compounds such as polyamide or polyester.

FIG. **2**A and FIG. **2**B are schematic views showing a process that an ink composition is adhered to the surface of a base material such as a glass substrate or ceramics substrate and a solvent evaporates from a droplet of the ink composition.

Specifically, when an ink composition **203** is adhered to a surface **202** of a base material **201**, the surface area (S) of an interface **204**, which is in contact with a gas phase, of the ink composition **203** is kept to have the minimum ratio (S/V) to the volume (V) of the ink composition **203**, in other words, the ratio (V/S) between the volume (V) of the ink composition **203** and the surface area (S) of the interface **204** is controlled to be kept at a maximum as shown in FIG. **2**A. But, as the solvent evaporates from the ink composition, the minimum ratio between the surface area of the interface **204**, which is in contact with the gas phase, of the ink composition **203** and the volume of the ink composition **203** cannot be kept, and the ratio of the surface area of the interface **204**, which is in contact with the gas phase, of the ink composition **203** to the volume of the ink composition increases as shown in FIG. **2**B. More specifically, the middle of the ink composition **203** adhered to the surface **202** of the base material **201** sinks toward the base material **201**, and the ratio of the surface area of the interface **204**, which is in contact with the gas phase, of the ink composition **203** to the volume of the ink composition increases as shown in FIG. **2**B. And, a pigment **205** contained in the ink composition **203** is concentrated toward portions (circumference) **206*a*** and **206*b*** of the interface of the ink composition **203**, and the uniform dispersion of the pigment **205** within the ink composition **203** is lost. Therefore, a pattern formed by the adhesion of the pigment **205** to the surface **202** of the base material **201** has light and dark portions. And, it is hard to stably form a good pattern because the adhesive force to the surface of the substrate is partly different.

The inventors have repeated various experiments, and finally found an ink composition which forms a good pattern without involving the above-described disadvantages by selecting types and particle diameters of a pigment as the coloring matter, a dispersant, and a solvent. In the experiments, respective steps shown in Table 1 were taken into account.

TABLE 1

	Conventional ink composition	Ink composition to provide good pattern
A. Surface of base material	Droplets deform	Droplet shape is substantially constant
B. Solvent evaporates	Further deforms	Droplet shape is not deformed heavily
C. Most solvent has evaporated	Weak adhesion of pigment	Pigment adheres firmly to base material

It is apparent from Table 1 that in order to form a good pattern, when the solvent evaporates from the ink composition adhered to the surface of the base material, the shape of droplets of the ink composition on the surface of the base material must be kept to have the base material wet with the droplets. And, the pigment contained in the ink composition is required to have an affinity for the surface of the base material and a high adhesive force.

To meet such conditions, various experiments have been made to find materials for the ink composition, and the results obtained are shown in Table 2 and Table 3. Symbols ○, Δ and × in Table 2 and Table 3 indicate a good level, a practical level and an unpractical level, respectively.

TABLE 2

Materials for ink composition			State of ink composition adhered to base material		
No.	Solvent	Dispersant	Repellency	Spreading	Adhesive force
1	Water	Nonionic surface active agent	Δ ~ o	X	X
2	Water	Anionic surface active agent	Δ ~ o	X	X
3	Water	Cationic surface active agent	Δ ~ o	X	X

TABLE 3

	Materials for ink composition			State of ink composition adhered to base material		
No.	Solvent	Dispersant	Additive	Repelling	Spreading	Adhesive force
1	Alcohol	Polyvinyl butyral	Polycarboxylic acid	○	○	○
2	Alcohol	Polyvinyl pyridine	Silicone oil	○	○	○

TABLE 3-continued

No.	Materials for ink composition: Solvent	Dispersant	Additive	State of ink composition adhered to base material: Repelling	Spreading	Adhesive force
3	Alcohol	Polyvinyl alkyl pyrrolidone	Acrylic resin	○	Δ	Δ
4	Alcohol	Acrylic resin	Silicone resin	○	Δ~○	○
5	Methyl ethyl ketone/toluene	Polyester resin	Polycarboxylic acid	○	○	○
6	Methyl ethyl ketone/toluene	Polyurethane resin	Silicone resin	○	Δ	○
7	Methyl ethyl ketone/toluene	Acrylic resin	Modified polysiloxane copolymer	○	Δ	○
8	Water	Acrylic resin (Base material temperature: 65° C.)	Fluorine-based surface active agent	○	○	○
9	Water	Acrylic resin	Polyether modified silicone oil	○	○	○
10	Water	Acrylic resin	Sodium dialkyl sulfosuccinate	○	○	○
11	Water	Polyvinyl alkyl pyrrolidone	Polyether modified silicone oil	○	○	○
12	Water	Polyvinyl alkyl pyrrolidone	Polyether modified silicone oil	○	○	○

Table 2 shows the results obtained when conventional ink compositions were adhered to a glass substrate, and Table 3 shows the results also obtained when the ink composition of the present invention was adhered to a glass substrate. FIG. **1**B and FIG. **1**D are photographs taken through a light microscope to show a state that a conventional ink composition is adhered to a glass substrate, and FIG. **1**A and FIG. **1**C are photographs taken through a light microscope to show a state that the ink composition of the invention is adhered to a glass substrate. FIG. **1**A and FIG. **1**B show a state that droplets are widely spaced as an experiment in order to clarify the effects of the ink composition of the present invention, and FIG. **1**C and FIG. **1**D show an example of drawing a line by continuously ejecting. It is apparent from FIG. **1**A and FIG. **1**B that the ink composition of the present invention has its all droplets arranged in good order with their shapes kept same, but the droplets of the conventional ink composition are deformed and not arranged in good order. And, it is apparent from FIG. **1**C and FIG. **1**D that the center of the line formed of the conventional ink composition has a portion lighter than its surroundings. In other words, it is apparent from FIG. **1**A to FIG. **1**D that the ink composition according to the invention can form a good pattern stably on the surface (a to-be-colored layer) of the base material which is of the glass substrate and different from fiber of paper or the like. The same result can also be obtained when the surface of the basic material is a ceramics substrate or a film made of polyester resin or the like.

Now, the ink composition of the present invention will be described in detail.

The ink composition of the present invention contains a solvent, a pigment, and a dispersant which enhances the dispersion of the pigment into the solvent. By appropriately controlling the types, amounts and component ratios of the solvent, pigment and dispersant, after adhering droplets of the ink composition onto the surface of a base material, the ratio (S/V) of the surface area (S) of the interface, which is in contact with the gas phase, of the droplets to the volume (V) of the droplets is kept minimum, in other words, the ratio (V/S) between the volume (V) of the droplets and the surface area (S) of the interface is kept maximum while the solvent is evaporating from the droplets. Therefore, while the solvent is evaporating from the droplets, the pigment contained in the droplets is kept uniformly dispersed within the droplets. And, when the ink composition has physical properties such as a surface tension of 20.0 dyn/cm to 50.0 dyn/cm at 25° C. and a viscosity of 1.5 cp to 20.0 cp at 25° C., in a process that the solvent is evaporating from the droplets after adhering onto the surface of the base material, the ratio (S/V) of the surface area (S) of the interface, which is in contact with the gas phase, of the droplets to the volume (V) of the droplets can be kept minimum, in other words, the ratio (V/S) between the volume (V) of the droplets and the surface area (S) of the interface can be kept maximum, and the pigment contained in the droplets can be kept uniformly dispersed within the droplets. Besides, the ink composition of the invention contains a solvent, a pigment, and a dispersant which enhances the dispersion of the pigment into the solvent, and an additive can be added in addition to the solvent, pigment and dispersant in order to keep the ratio (S/V) of the surface area (S) of the interface, which is in contact with the gas phase, of the droplets to the volume (V) of the droplets minimum, in other words, keep maximum the ratio (V/S) between the volume (V) of the droplets and the surface area (S) of the interface in a process that the solvent is evaporating from the droplets after adhering the ink composition in the form of droplets onto the surface of the base material, and also to control the ink composition to have physical properties such as a surface tension of 20.0 dyn/cm to 50.0 dyn/cm at 25° C. At this time, the physical properties of the ink composition is adjusted to have a viscosity of 1.5 cp to 20.0 cp at 25° C. Therefore, the ink composition according to the invention can form a good pattern stably without causing light and dark portions or a partly different adhesive force of the pigment.

In the ink composition according to the invention, the affinity of the solvent for the surface of the base material and its evaporation rate have a significant effect on steps A and B in Table 1. In other words, to accurately position the ink composition on the surface of the base material, the solvent needs to have an affinity for the surface of the base material

to obtain appropriate wettability and an appropriate evaporation rate as well.

To meet such conditions, the solvent for the ink composition of the invention can be a mixture of water and various types of organic solvents to be used solely or as a mixture. Preferably usable organic solvents are at least one member selected from a group consisting of alkyl alcohols having 1 to 4 carbon atoms such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol and isobutyl alcohol; amides such as dimethylformamide and dimethylacetamide; ketones or ketoalcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols containing alkylene groups of two to six carbon atoms such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexylene glycol, and diethylene glycol; lower alkyl ethers of polyhydric alcohol such as ethylene glycol methyl ether, ethylene glycol ethyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethylene ether; and esters such as ethyl acetate and butyl acetate. To use a plurality of solvents in a mixed form, a combination and a mixing ratio of the solvents are determined in a range that the properties of the ink composition are not deteriorated. The ink composition using water only as the solvent is defined as a water-based ink composition, and one using an organic solvent as the solvent is defined as a solvent-based ink composition.

And, to stably form a good pattern without causing light and dark portions or a partly different adhesive force of the pigment, the pigment for the ink composition of the invention is desired to have an average particle diameter of 0.001 μm to 0.30 μm, preferably 0.05 μm to 0.15 μm, in view of the transparency of the pattern to be formed, and 0.5 μm to 50 μm, preferably 1 μm to 20 μm in view of securing a luminous efficacy for a phosphor. The average particle diameter is used to indicate as a diameter of the smallest sphere having the same surface area.

The pigment for the ink composition of the invention can be various types depending on where it is used. And examples include inorganic pigments such as carbon black, graphite black, iron black, Cu—Fe—Mn black, Co—Fe—Cr black, Cu—Cr—Mn black, titanium black, manganese black, cobalt black, ultramarine blue, cobalt blue, red oxide, cadmium red, cobalt green, sulfide phosphor, rare earth oxide phosphor, and rare earth oxysulfide phosphor; and organic pigments such as azo-based pigment, phthalocyanine-based pigment, indigo-based pigment, anthraquinone-based pigment, perylene-based pigment, perinone-based pigment, dioxazine-based pigment, quinacridone-based pigment, isoindorinone-based pigment, phthalone-based pigment, methine-azomethine-based pigment, and condensed polycyclic pigment. And, these pigments can be used solely or in a mixed form. To disperse an organic pigment into the solvent-based ink composition, a combination of the organic solvent and the organic pigment shall be selected so that the organic pigment does not dissolve into the organic solvent.

When the ink composition of the invention is to be applied for a color filter for the LCD, it is preferable to use copper phthalocyanine blue as a blue pigment, dioxazine violet as a purple pigment, anthraquinone red or perylene red as a red pigment, isoindorine yellow, benzidine yellow or isoindorinone yellow as a yellow pigment, phthalocyanine green as a green pigment, and carbon black, iron black, Cu—Fe—Mn black, Co—Fe—Cr black or Cu—Cr—Mn black as a black pigment. And, when the ink composition of the invention is to be applied for a color filter for a color image receiving tube/PDP, it is preferable to use ultramarine blue or cobalt blue as a blue pigment, red oxide or cadmium red as a red pigment, cobalt green as a green pigment, and carbon black, iron black, graphite black, titanium black or cobalt black as a black pigment. Furthermore, when the ink composition of the invention is to be applied for C-CRT/PDP phosphor picture elements, it is preferable to use Zn:Ag as a blue-luminous phosphor, Y_2O_2S:Eu or Y_2O_3:Eu as a red-luminous phosphor, ZnS:Cu, ZnS:Cu or Au as a green-luminous phosphor.

Besides, the dispersant for the ink composition of the invention must be dispersed into the solvent so that it is adsorbed to the pigment to prevent the pigments from coagulating mutually, and it is also required to have a high affinity for a glass substrate. The dispersant which is adsorbed into the surface of the pigment contained in the ink composition serves to uniformly disperse the pigment into the ink composition, and also firmly adheres the pigment onto the surface of the base material. Therefore, the dispersant is related to step A in Table 1 and has a significant effect on step C.

To meet the above-described conditions, the dispersant for the ink composition of the invention is determined in view of combinations of the above-described ink composition types/pigments as required. Specifically, for a combination of the water-based ink composition/organic pigment, the dispersant usable can be, for example, acrylic resin, polyvinyl acrylic pyrrolidone and polyvinyl alkyl pyrrolidone. Similarly, the dispersant suitably usable is acrylic resin, polyvinyl alkyl pyrrolidone and the like when a combination of the ink composition type and the pigment is a water-based/inorganic pigment; the dispersant is polyvinyl butyral, acrylic resin, polyvinyl pyridine, polyamide resin, phenol resin, polyvinyl acrylic pyrrolidone, polyurethane resin and polyester resin when the combination is a solvent-based/organic pigment; and the dispersant is polyvinyl butyral, acrylic resin and polyvinyl acrylic pyrrolidone when the combination is a solvent-based/inorganic pigment. When an organic solvent is to be used as the solvent in the ink composition of the present invention, it is more preferable to use alcohols. When alcohols are used as the organic solvent, the dispersant suitably usable includes polyvinyl butyral, acrylic resin, polyvinyl pyridine, polyamide resin, phenol resin or polyvinyl acrylic pyrrolidone when the pigment is an organic pigment. On the other hand, when an inorganic pigment is to be used, polyvinyl butyral, acrylic resin or polyvinyl acrylic pyrrolidone can be used suitably.

Furthermore, the ink composition of the invention may contain an additive as a component for the ink composition in order to keep the ratio (S/V) of the surface area (S) of the interface, which is in contact with the gas phase, of the droplets to the volume (V) of the droplets minimum, in other words, keep maximum the ratio (V/S) between the volume (V) of the droplets and the surface area (S) of the interface in a process that the solvent is evaporating from the droplets after adhering the ink composition in the form of droplets onto the surface of the base material. When the additive is used, the physical properties of the ink composition can be controlled to have a surface tension of about 20.0 dyn/cm to about 50.0 dyn/cm at 25° C.

The additive for the ink composition of the invention is suitably determined according to the above-described types of the ink composition. Specifically, when the ink composition is water-based, the additive preferably usable is at least one member selected from a group consisting of

sodium dialkyl sulfosuccinate, fluorine-based surface active agent, and polyether modified silicone oil. And, when the ink composition is solvent-based, the additive preferably usable is at least one member selected from a group consisting of silicone resin, acrylic resin, modified polysiloxane copolymer, polycarboxylic acid, polyester carboxylate, and unsaturated polycarboxylic acid.

And, as to the ratio of the pigment in the ink composition, it is 1 to 30 parts by weight, and preferably 3 to 15 parts by weight, to 100 parts by weight of the solvent to prevent a nozzle from being clogged by the ink composition and in view of an optical density (OD) of the pattern to be formed.

On the other hand, it is preferable that the dispersant is 1 to 100 parts by weight and the additive is 1 to 30 parts by weight with respect to 100 parts by weight of the pigment. It is more preferable that the dispersant is 10 to 30 parts by weight and the additive is 3 to 10 parts by weight with respect to 100 parts by weight of the pigment.

When the dispersant is less than 1 part by weight to 100 parts by weight of the pigment, the dispersion of the pigment is degraded, causing it difficult to obtain the ink composition in which the pigment is uniformly dispersed. And, when the dispersant exceeds 100 parts by weight to 100 parts by weight of the pigment, the ink composition has a high viscosity, and the ink is not ejected uniformly from a nozzle in the ink-jet method, so that it is difficult to form a good pattern.

And, when the additive is less than 1 part by weight and exceeds 30 parts by weight with respect to 100 parts by weight of the pigment, in a process that the solvent is evaporating from the droplets after adhering the ink composition in the form of droplets onto the surface of the base material, it is difficult to control to minimize the ratio (S/V) of the surface area (S) of the interface, which is in contact with the gas phase, of the droplets to the volume (V) of the droplets, in other words, maximize the ratio (V/S) of the volume (V) of the droplets to the surface area (S) of the interface.

In addition, to the ink composition of the invention, it is possible to add various types of components in a range not deteriorating the properties of the ink composition as required, such as a pH adjustor, a mildewproofing agent, a chelating agent or a reducing agent.

A pattern forming method according to the present invention uses the above-described ink composition to form a pattern on the surface of a base material by the ink-jet method. In the pattern forming method according to the present invention, the ink-jet method for ejecting the ink composition may be any method which can adhere the droplets of the ink composition onto the surface of a base material by effectively ejecting the ink composition from a nozzle. Suitably usable examples of the ink-jet method which ejects the ink composition include an electrostatic attraction method which applies an intense electrical field between a nozzle and an accelerating electrode provided several millimeters before the nozzle to change the ink composition to particles and extract successively from the nozzle and gives an information signal to deflecting electrodes while the extracted ink composition is flying between the deflecting electrodes to form a pattern; a method which applies a high pressure to ink by a small pump and mechanically vibrates a nozzle by a quartz oscillator or the like to forcedly eject the droplets of the ink composition, electrically charges the ejected droplets according to an information signal when they are ejected, and allows the charged droplets between deflecting electrode plates to deflect them according to a charged level, thereby forming a pattern; a method which gives an electrical signal to a piezoelectric element to cause a mechanical displacement to apply a pressure to the ink composition, and eject the droplets of the ink composition from a nozzle; and a method which applies thermal energy to the ink composition to cause a sharp volume change in the ink composition to eject the droplets of the ink composition from a nozzle.

Furthermore, in the case of forming a pattern of picture elements for a color filter, it is desired to control the amount of the droplets of the ink composition to be adhered to the surface of a base material. Specifically, if the amount of the droplets of the ink composition to be adhered to the surface of the base material is small, the amount of the pigment adhered to the surface of the base material is small, so that the optical density (OD) of the pattern formed is low, and it is hard to obtain prescribed optical properties. And, to remedy such a disadvantage, the amount of the pigment contained in the ink composition may be increased, thereby improving the optical density (OD) of the pattern. However, doing so makes it difficult to keep the properties of the ink composition and the nozzle tends to be clogged with the ink composition. Thus, the disadvantages cannot be remedied practically. On the other hand, if the amount of the droplets of the ink composition to be adhered to the surface of a base material is large, even if the amount of the pigment contained in the ink composition is decreased, the solvent contained in the ink composition is slow to evaporate in a moist atmosphere in the rainy season or the like and in a low-temperature environment in winter or the like, so that the adhesion of the pigment onto the surface of the base material is lowered, and it is hard to form a good pattern stably.

When a water-based ink composition is used in the pattern forming method according to the invention, it is desired to keep the surface of the base material, to which the droplets of the ink composition are adhered, at 20° C. to 120° C. in view of controlling the evaporation rate of the solvent water.

The color filter according to the present invention has a base material and a colored layer which has a pigment adhered to the surface of the base material by the ink-jet method. And, this base material can be the above-described various types of base materials. Their examples include a glass substrate or a ceramics substrate; various types of film materials such as polyester resin, diacetate resin, triacetate resin, acrylic resin, polycarbonate resin, polyvinyl chloride resin, polyimide resin, cellophane or celluloid; and coated paper of which the surface is coated with organic polymer compounds such as polyamide or polyester. And, they can be applied for a display unit such as LCD, CRT or PDP, a wafer having a solid state image pickup device such as the light receiving face of a camera tube, CCD, BBD, CID or BASIS, and a contact image sensor using a thin film semiconductor. And, the pigment which forms the colored layer on the surface of the base material can be the above-described various types of pigments.

The colored layer for the color filter according to the present invention is formed by adhering the above-described ink composition onto the surface of the base material by the ink-jet method and adhering the pigment contained in the ink composition onto the surface of the base material. The thickness of the colored layer of the color filter is determined according to a desired spectral characteristics, but generally desired to be about 0.01 to 5 μm.

The colored layer itself for the color filter according to the invention has a sufficient durability, but to protect the

colored layer from various environmental conditions, a resin of polyamide, polyimide, polyurethane, polycarbonate or silicone or an inorganic film of Si_3N_4, SiO_2, SiO, Al_2O_3 or Ta_2O_3 can be formed as a protective layer on the surface of the colored layer by an application method such as spin coating or roll coating or a deposition method. When the provided protective layer is oriented, it can be applied to LCD easily.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1A** is a photograph taken through a light microscope to show a state that the ink composition of the invention is adhered to a glass substrate.

FIG. **1B** is a photograph taken through a light microscope to show a state that a conventional ink composition is adhered to a glass substrate.

FIG. **1C** is a photograph taken through a light microscope to show a state that the ink composition of the invention is adhered to a glass substrate.

FIG. **1D** is a photograph taken through a light microscope to show a state that a conventional ink composition is adhered to a glass substrate.

FIG. **2A** is a schematic view showing a state that an ink composition is adhered to the surface of a glass substrate or ceramics substrate.

FIG. **2B** is a schematic view showing a state that a solvent is evaporating from a droplet of the ink composition.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the invention will be described in detail with reference to the accompanying drawings. In the following embodiments, the symbol "%" indicates a percent by weight.

Embodiment 1

In accordance with compositions A to C shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink compositions A to C. The pigment in the ink compositions A to C has an average particle diameter of about 0.1 μm. And, Table 5 shows viscosities and surface tensions of the ink compositions A to C at 25° C. Solmix AP-4 is sold by Nippon Kasei Chemical Co., Ltd.

A glass substrate (with black matrix formed) for the display of LCD was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi), and a color filter was produced using the ink compositions A to C.

And, the obtained color filter had a good pattern with a black matrix (BM) width of about 40 μm and a pattern width of about 140 μm of each formed colored layer. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was good, and heat resistance, cold resistance and chemical resistance were equal to those of the colored layer of a conventional color filter formed by a dyeing method, a pigment dispersing method, an electrodeposition method or a printing method. Besides, optical properties of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer was about one fifth of the cost of forming the colored layer of the conventional color filter.

Embodiment 2

In accordance with compositions D to F shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink compositions D to F. The pigment in the ink compositions D to F has an average particle diameter of about 0.1 μm. And, Table 5 shows the viscosities and surface tensions of the ink compositions D to F at 25° C.

The same glass substrate as used in Embodiment 1 was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi), and a color filter was produced using the ink compositions D to F.

And, the obtained color filter had a good pattern with a black matrix (BM) width of about 40 μm and a pattern width of about 140 μm of each formed colored layer. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was also good as in Embodiment 1, and heat resistance, cold resistance and chemical resistance were equal to those of the colored layer of a conventional color filter formed by a dyeing method, a pigment dispersing method, an electrodeposition method or a printing method. Besides, optical properties of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer was about one fifth of the cost of forming the colored layer of the conventional color filter.

Embodiment 3

In accordance with composition G shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink composition G. The pigment in the ink composition G has an average particle diameter of about 0.25 μm. And, Table 5 shows the viscosity and surface tension of the ink composition G at 25° C.

The same glass substrate (without the BM) as used in Embodiment 1 was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi), and a color filter was produced using the ink compositions A to C and G.

And, the obtained color filter had a good pattern with a black matrix (BM) width of about 40 μm and a pattern width of about 140 μm of each formed colored layer. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was good, and heat resistance, cold resistance and chemical resistance were equal to those of the colored layer of a conventional color filter formed by a dyeing method, a pigment dispersing method, an electrodeposition method or a printing method. Besides, optical properties of the colored layer were also same to those of the colored layer of the conventional color filter.

Embodiment 4

In accordance with compositions H to J shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink compositions H to J. The pigments in the ink compositions H to J have an average particle diameter of about 0.023 μm, about 0.020 μm and about 0.021 μm. And, Table 5 shows viscosities and surface tensions of the ink compositions H to J at 25° C.

A screen glass substrate (Nippon Electric Glass Co., Ltd.; with black matrix formed) for a 28-inch wide C-CRT was mounted on a piezoelectric type ink-jet printer (MJ-800C;

Seiko Epson Corp.; 720 dpi), and a pattern of a colored layer of a color filter was produced using the ink compositions H to J.

Thus, a color filter obtained had a pattern of each colored layer formed in black stripe holes having a pattern width of 150 μm. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was good, and heat resistance, cold resistance and chemical resistance of the each colored layer were equal to those of a conventional colored layer formed by a photolitho method. Besides, optical properties such as luminous brightness of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer including facilities investment was about 1/100 of the cost of forming the conventional colored layer. And, the amount of materials used for the colored layer was about 1/30.

Embodiment 5

In accordance with compositions K to M shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink compositions K to M. The pigments in the ink compositions K to M have an average particle diameter of about 0.023 μm, about 0.020 μm and about 0.021 μm. And, Table 5 shows viscosities and surface tensions of the ink compositions K to M at 25° C.

The same screen glass substrate as used in Embodiment 4 was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi), and a pattern of a colored layer for a color filter was produced using the ink compositions K to M.

Thus, a color filter obtained had a pattern of each colored layer formed in black stripe holes having a pattern width of 150 μm. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was good, and heat resistance, cold resistance and chemical resistance of the each colored layer were equal to those of a conventional colored layer formed by a photolitho method. Besides, optical properties such as luminous brightness of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer including facilities investment was about 1/100 of the cost of forming the conventional colored layer. And, the amount of materials used for the colored layer was about 1/30.

Embodiment 6

In the same way as in Embodiment 4, the ink compositions H to J were prepared.

A screen glass substrate (Asahi Glass Co., Ltd.) for a 28-inch plasma display was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi), and a pattern of a colored layer of a color filter was produced using the ink compositions H to J.

Thus, a color filter obtained had a pattern of each colored layer formed in rectangular holes having a pattern width of 150 μm. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was good, and heat resistance, cold resistance and chemical resistance of the each colored layer were equal to those of a conventional colored layer formed by a photolitho method. Besides, optical properties such as luminous brightness of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer including facilities investment was about one fifth of the cost of forming the conventional colored layer. And, the amount of materials used for the colored layer was about 1/20.

Embodiment 7

In accordance with compositions N to P shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink compositions N to P. The pigments in the ink compositions N to P have an average particle diameter of about 0.023 μm, about 0.020 μm and about 0.021 μm. And, Table 5 shows viscosities and surface tensions of the ink compositions N to P at 25° C.

A screen glass substrate (Asahi Glass Co., Ltd.) for a 28-inch plasma display was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi), and a pattern of a colored layer of a color filter was produced using the ink compositions N to P.

Thus, a color filter obtained had a pattern of each colored layer formed in rectangular holes having a pattern width of 150 μm. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the glass substrate and the each colored layer was good, and heat resistance, cold resistance and chemical resistance of the each colored layer were equal to those of a conventional colored layer formed by a photolitho method. Besides, optical properties such as luminous brightness of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer including facilities investment was about one fifth of the cost of forming the conventional colored layer. And, the amount of materials used for the colored layer was about 1/20.

Embodiment 8

In accordance with compositions Q to S shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink compositions Q to S. The pigments in the ink compositions Q to S have an average particle diameter of about 0.010 μm. And, Table 5 shows viscosities and surface tensions of the ink compositions Q to S at 25° C.

A wafer with a CCD (Charge Coupled Device) formed was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi). And, to provide a pattern of each colored layer for a color filter in correspondence with each photo cell of the CCD, a pattern of a colored layer for the color filter was produced using the ink compositions Q to S.

Thus, a color filter obtained had a pattern of each colored layer having a pattern width of 150 μm. On this color filter, the maximum difference among pattern widths of the formed colored layer was about 10 μm.

Adhesion between the wafer and the each colored layer was good, and heat resistance, cold resistance and chemical resistance of the each colored layer were equal to those of a conventional colored layer formed by a photolitho method. Besides, optical properties of the colored layer were also same to those of the colored layer of the conventional color filter.

The cost of forming the colored layer including facilities investment was about 1/100 of the cost of forming the conventional colored layer. And, the amount of materials used for the colored layer was about 1/30.

Embodiment 9

In accordance with composition T shown in Table 4, respective components were mixed and stirred in a stirring bath adjusted to 20° C., and passed through a filter having a pore diameter of 0.5 μm to prepare the ink composition T.

The pigment in the ink composition T has an average particle diameter of about 0.025 μm. And, Table 5 shows the viscosity, surface tension and density of the ink composition T at 25° C.

A polyester-based OHP film was mounted on a piezoelectric type ink-jet printer (MJ-800C; Seiko Epson Corp.; 720 dpi). And, a character pattern was formed on the OHP by using the ink composition T.

Thus, the OHP film obtained has the character pattern having a pattern width of 250 μm. On this OHP film, the maximum difference among the formed character pattern widths was about 15 μm.

Adhesion between the OHP film and the colored layer forming the character patterns was good, and heat resistance, cold resistance and chemical resistance of the colored layer were equal to those of a conventional colored layer formed on an OHP film. Besides, optical properties of the colored layer such as OD were also same to those of the conventional colored layer.

The cost of forming the colored layer for the character patterns including facilities investment was about 1/100 of the cost of forming the conventional colored layer.

TABLE 4

Ink Composition	Solvent (wt %)	Pigment (wt %)	Dispersant (wt %)	Additive (wt %)
A	Solmix AP-4 (94)	Phthalocyanine blue (3)	Polyvinyl butyral (3)	—
B	Solmix AP-4 (94)	Anthraquinone red (3)	Polyvinyl pyridine (3)	—
C	Methyl ethyl ketone (50)/ toluene (44)	Phthalocyanine green (3)	Polyester resin (3)	—
D	Water (92)	Phthalocyanine green (4)/ Benzidine yellow (1)	Polyvinyl acrylic pyrrolidone (3)	—
E	Water (91)	Perylene red (3)	Polyvinyl acrylic pyrrolidone (3)	Sodium dialkyl sulfosuccinate (3)
F	Water (93.5)	Phthalocyanine blue (2.7)/ Dioxazine violet (0.3)	Acrylic resin (3)	Fluorine-based surface active agent (0.5)
G	Solmix AP-4 (87)	Iron black (10)	Polyvinyl butyral (3)	—
H	Solmix AP-4 (88)	Cobalt blue (10)	Polyvinyl butyral (2)	—
I	Solmix AP-4 (90)	Red oxide (8)	Polyvinyl acrylic pyrrolidone (2)	—
J	Toluene (50)/ buthylacetate (38)	Cobalt green (10)	Acrylic resin (2)	—
K	Water (85)	Ultramarine blue (10)	Acrylic resin (2)	Sodium dialkyl sulfosuccinate (3)
L	Water (80)	Codmium sulfide (8)	Acrylic resin (2)	Polyether modified silicone oil (10)
M	Water (79)	Cobalt green (10)	Polyvinyl acrylic pyrrolidone (3)	Polyether modified silicone oil (8)
N	Solmix AP-4 (85)	Ultramarine blue (10)	Polyvinyl butyral (3)	Acrylic resin (2)
O	Solmix AP-4 (88)	Cadmium sulfide (8)	Acrylic resin (2)	Silicone resin (2)
P	Toluene (50)/ ethylacetate (36)	Cobalt green (10)	Polyvinyl acrylic pyrrolidone (3)	Polycarboxylic acid (1)
Q	Water (87)	Phthalocyanine green (5)	Polyvinyl acrylic pyrrolidone (5)	Sodium dialkyl sulfosuccinate (3)
R	Water (89)	Anthraquinone red (3)	Polyvinyl acrylic pyrrolidone (3)	Polyether modified silicone oil (5)

TABLE 4-continued

Ink Composition	Solvent (wt %)	Pigment (wt %)	Dispersant (wt %)	Additive (wt %)
S	Water (93.5)	Phthalocyanine blue (3)	Polyvinyl acrylic pyrrolidone (3)	Fluorine-based surface active agent (0.5)
T	Water (86.5)	Co—Fe—Cr black (10)	Acrylic resin (3)	Fluorine-based surface active agent (0.5)

TABLE 5

Ink composition	Viscosity (cp)	Surface tension (dyn/cm)
A	4	22
B	5	22
C	5	28
D	8	29
E	3	31
F	3	31
G	9	22
H	7	22
I	8	22
J	5	28
K	6	30
L	10	30
M	15	32
N	12	30
O	7	27
P	12	30
Q	7	36
R	4	40
S	3	42
T	11	28

As described above, when the ink composition according to the present invention is used, the pigment is uniformly dispersed in the droplets adhered onto the surface of glass, ceramics or polyester resin of a base material. Therefore, a fine pattern can be formed on the surface of glass, ceramics or polyester resin by the ink-jet method without forming a to-be-colored layer.

According to the pattern forming method of the present invention, a pattern is formed by the ink-jet method using the ink composition containing the pigment which is uniformly dispersed in the droplets adhered onto the surface of glass, ceramics or polyester resin of a base material, so that a fine pattern having high reliability can be formed indirectly onto the surface of glass, ceramics or polyester resin of the base material. Therefore, the number of processes and facilities investment can be decreased and the pattern can be formed on the base material economically.

Besides, since the color filter of the present invention has the colored layer formed of the pigment adhered onto the surface of a base material by the ink-jet method, practical reliability in optical resistance and water resistance and cost efficiency can be improved.

What is claimed is:

1. A method of forming a pattern on a base material selected from glass and ceramic by an ink jet method, comprising the steps of:

preparing an ink composition by uniformly dispersing a pigment in a solvent with a dispersant for enhancing an affinity between the solvent and the pigment;

ejecting the ink composition onto a surface of a base material through a nozzle by the ink jet method to form a droplet of the ink composition on the surface of the base material, wherein the droplet is formed such that the ratio of a volume of the droplet to a surface area of the droplet, except an area contacting the base material, is substantially maximized;

evaporating the solvent from the droplet while keeping the ratio substantially at the maximum; and

adhering the pigment onto the base material to form a pattern.

2. The method of claim **1**, wherein the method further comprises a step of filtering the ink composition to control an average of the pigment in the ink composition to from 0.001 μm to 0.3 μm.

3. The method of claim **1**, wherein the base material is a glass substrate and the ink composition is controlled to have a surface to tension of 20 dyn/cm to 32 dyn/cm at 25° C. and viscosity of 3 cp to 20 cp at 25° C.

4. The method of claim **2**, wherein the base material is a glass substrate and the ink composition is controlled to have a surface to tension of 20 dyn/cm to 32 dyn/cm at 25° C. and viscosity of 3 cp to 20 cp at 25° C.

5. A method of forming a pattern on a base material selected from glass an ceramic by an ink jet method, comprising the steps of:

preparing an ink composition having a surface tension of 20 dyn/cm to 50 dyn/cm at 25° C. and viscosity of 1.5 cp to 20 cp at 25° C., by uniformly dispersing a pigment in a solvent with a dispersant for enhancing an affinity between the solvent and the pigment;

ejecting droplets of the ink composition through a nozzle using an ink-jet method onto the base material, wherein each of the droplets is formed such that the ratio of a volume of the droplet to a surface area of the droplet, except an area contacting the base material, is substantially maximized; and

evaporating the solvent in the ink composition of the droplets, while substantially keeping the ratio of the volume to the surface area of the droplet, and thereby adhering the pigment on the base material to form a pattern.

6. The method of claim **5**, wherein the method further comprises a step of filtering the ink composition to control an average of the pigment in the ink composition to from 0.001 μm to 0.3 μm.

7. The method of claim **5**, wherein the method further comprises an additive for controlling the surface tension of the droplet.

8. The method of claim **5**, wherein said base material is a glass substrate and said ink composition is controlled to have a surface tension of 20 dyn/cm to 32 dyn/cm at 25° C. and viscosity of 3 cp to 20 cp at 25° C.

9. The method of claim **5**, wherein said solvent is water, said pigment is an organic substance, and said dispersant is

at least one member selected from a group consisting of acrylic resin, polyvinyl acrylic pyrrolidone and polyvinyl alkyl pyrrolidone.

10. The method of claim **5**, wherein said solvent is water, said pigment is an inorganic substance, and said dispersant is at least one member selected from a group consisting of acrylic resin and polyvinyl acrylic pyrrolidone.

11. The method of claim **5**, wherein said solvent is an organic solvent or a mixture of water and an organic solvent, said pigment is an organic substance, and said dispersant is at least one member selected from a group consisting of polyvinyl butyral, acrylic resin, polyvinyl pyridine, polyamide resin, phenol resin, polyvinyl acrylic pyrrolidone, polyurethane and polyester resin.

12. The method of claim **5**, wherein said solvent is an organic solvent or a mixture of water and an organic solvent, said pigment is an inorganic substance, and said dispersant is at least one member selected from a group consisting of polyvinyl butyral, acrylic resin, and polyvinyl acrylic pyrrolidone.

13. A method of manufacturing a color filter comprising a substrate selected from a glass substrate or ceramic substrate and a color layer formed on the substrate, said method comprising the steps of:

preparing an ink composition comprising a pigment, a solvent, and a dispersant such that the ink composition has a surface tension of 20 dyn/cm to 50 dyn/cm at 25° C. and viscosity of 1.5 cp to 20 cp at 25° C.;

ejecting the ink composition through a nozzle using the ink jet method onto the substrate to form a droplet of the ink composition adhered on the substrate, the droplet being formed such that the ratio of a volume of the droplet to a surface area of the droplet, except an are contacting the substrate, is substantially at a maximum; and

evaporating the solvent in the ink composition of the droplets while keeping the ratio substantially at a maximum, thereby forming a pattern of the coloring layer which is adhered on the substrate.

14. The method of claim **13**, wherein said substrate is a glass substrate and said ink composition has a surface tension of 20 dyn/cm to 32 dyn/cm at 25° C. and viscosity of 3 cp to 20 cp at 25° C.

15. The method of claim **13**, wherein said substrate is a wafer on which a charge coupled device is formed.

16. A display unit having a color filter manufactured by the method of claim **13**.

17. A solid state pickup device having a color filter manufactured by the method of claim **13**.

18. A method of manufacturing a color filter comprising a glass substrate and a color layer formed on the glass substrate, said method comprising the steps of:

preparing an ink composition comprising a pigment, a solvent, and a dispersant such that the ink composition has a surface tension of 20 dyn/cm to 32 dyn/cm at 25° C. and viscosity of 3 cp to 20 cp at 25°0 C.;

ejecting the ink composition through a nozzle using the ink jet method onto the glass substrate to form a droplet of the ink composition, wherein a shape of the droplet is formed such that a ratio of a surface area of the droplet, except an area contacting the substrate, to a volume of the droplet is substantially minimized; and

evaporating uniformly the solvent in the ink composition from the droplets while keeping the ratio substantially at a minimum, thereby forming a pattern of the coloring layer which is adhered on the substrate.

* * * * *

APPENDIX C

Related Proceedings

None